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THE FREEZING OF PURE LIQUIDS AND SOLUTIONS UNDER VARIOUS KINDS OF POSITIVE AND NEGATIVE PRESSURE AND THE SIMILARITY BETWEEN OSMOTIC AND NEGATIVE PRESSURE.

By C. S. Hudson.

1. Introductory Note.

In a recent article concerning the relation between osmotic pressure and negative pressure Professor Geo. A. Hulett[1] has shown that the lower vapor-pressure of solutions indicates that the solutions are under a negative pressure, and a calculation of the negative pressure that would cause the observed depression shows that this negative pressure is exactly equal to the osmotic pressure of the solution. This important conclusion is to my knowledge the first evidence that osmotic pressure has the same effect on liquids as does negative pressure.

The question occurred to me on reading Professor Hulett's article whether the lower freezing-temperatures of solutions can also be the result of osmotic pressure acting as a negative pressure. At first sight this does not appear probable, because, since it is known that a positive pressure causes the freezing-temperature of water to sink, it would seem that a negative pressure would cause a rise of freezing temperature and that solutions should freeze above zero rather than below. This reasoning is not correct, however, because the ice which freezes from a solution is under atmospheric pressure,

[1] Zeitschrift für physikalische Chemie, *42*, 361, 1903.

not negative pressure, and only the solution may properly be regarded as being under a negative pressure. The freezing-temperature of a liquid under such peculiar conditions of pressure is not known, and in order to calculate it I have investigated by thermodynamic methods the freezing of liquids under various kinds of pressure and this article presents the results of this inquiry. These results support without exception the view that osmotic pressure acts as a negative pressure.

2. INTRODUCTION.

In 1849 and 1850 James Thomson and Lord Kelvin showed by thermodynamic theory and by experiment that the freezing-temperature of water is lowered by a uniform pressure on the water and the ice to the extent of 0.00748° C. per atmosphere increase of pressure.

In 1881 J. H. Poynting [1] calculated from a thermodynamic cycle the change of freezing-temperature that is caused by an increase of pressure on the ice alone, such as might be realized for instance by the use of a rigid sieve in compressing the ice. Poynting showed that an increase of pressure of one atmosphere on the ice alone causes the freezing-temperature to sink 0.0899° C., a depression which is twelve times greater than that which is observed when the pressure is exerted uniformly on the water and the ice.

Recently it has been shown by G. N. Lewis [2] that if ice which is in equilibrium with water be subjected to a pressing [3] of dP, there will be no change of freezing-temperature provided the water is also subjected to the pressing dp that is fixed by the relation $dp/dP = V_i/V_w$, where V_i and V_w are the specific volumes of ice and water respectively. If these volumes are 1.0909 and 1.0001 cubic centimeters at 0°, $dp/dP = 1.09$; or, the increased pressing on the water must be nine per cent. greater than the increased pressing on the ice if the freezing-temperature is to remain unchanged. This relation can also be shown to result directly from a combination of

[1] Philosophical Magazine, (5), *12*, 32.

[2] Zeitschrift für physikalische Chemie, *38*, 207, 1901.

[3] I use the word *pressing* to signify a pressure that is exerted on one phase alone, in conformity with the use by Professor Ostwald of the German word *Pressung* to express the same idea.

the calculations of Thomson and Poynting. First, let the water and the ice be subjected to the pressing dp, on account of which the freezing-temperature sinks (0.00748) dp degrees. Let the pressing on the ice be now diminished by d_1p, the pressing on the water being meanwhile kept constant, as a result of which the freezing-temperature rises (0.0899) d_1p degrees. If the rise of the freezing-temperature be made equal to its previous fall there is finally no change of freezing-temperature and therefore $(0.0899)d_1p = (0.00748)dp$. The total increase of pressing on the ice is $dp - d_1p = dP$, and the elimination of d_1p from the two equations gives $dp/dP = 1.09$, which is the relation that has been stated by Lewis.

Our present knowledge of the change of freezing-temperature with change of pressure can be condensed to Thomson's and Poynting's statements, which include, as I have just shown, Lewis' statement; and it is possible to calculate from the two coefficients 0.00748 and 0.0899 alone the freezing-temperature of water under all conditions of small pressure. To illustrate by an example the method of such a calculation let us find what is the freezing-temperature of water that is under the pressing of two atmospheres when its ice is under the pressing of six atmospheres. Ice and water are in equilibrium under a uniform pressure of two atmospheres at $-2(0.00748)$ degrees, and if the pressing of four atmospheres in addition be applied to the ice alone the freezing temperature will sink 4 (0.0899) degrees farther; and therefore the final freezing-temperature is 0.375° C. below zero.

On the other hand it is also possible in case the freezing-temperature and the pressing on either the solid or the liquid phase are known to calculate the unknown pressing on the other phase. Let us consider in this connection the following calculation concerning the freezing-temperatures of dilute aqueous solutions. The exact experiments of Raoult and others have agreed in showing that the molecular depression of the freezing-temperature of water is very nearly 1.84 degrees. As we know that the pure ice which freezes from such solutions is under atmospheric pressure we can calculate what mechanical pressing on pure water would cause it to freeze at -1.84 degrees, or in other words to behave exactly as the dilute solution does in so far as freezing is concerned. If the pressure p is applied

uniformly to the ice and the water the freezing temperature sinks p (0.00748) degrees. If this pressure is removed from the ice but kept on the water the freezing-temperature rises p (0.0899) degrees. If the final depression of the freezing-temperature is 1.84 degrees we can write $p(0.00748) - p(0.0899) = 1.84$, and hence $p = -22.3$ [1] atmospheres. For comparison with this value let us calculate the pressure that would be exerted by a perfect gas if its volume, temperature, and molal concentration were those of the solution. One mol of a perfect gas occupying the volume of one liter at zero degrees would exert the pressure of 22.4 atmospheres, and if its temperature were lowered 1.84 degrees its pressure would decrease to 22.3 atmospheres. The identity of this pressure which a perfect gas would exert if its volume, temperature, and molal concentration were those of the solution with the mechanical pressure that must be exerted on pure water to make it freeze at the same temperature as does the solution is a striking and instructive fact. It is evident from this simple calculation that the freezing-temperatures of solutions indicate that the solutions are under a negative pressure.

But before discussing this subject further I wish to examine the reasoning which has led to the accepted values of the coefficients of Thomson and Poynting in order to make certain that the use of them in studying the properties of solutions is valid. I shall now describe a thermodynamic cyclic process which shows the change of freezing-temperature that accompanies any change of pressure on the ice and the water. This cyclic process is not different in principle from those described by Thomson and Poynting, but it is of wider application.

3. Thermodynamic Investigation of the Process of Freezing.

Let the following cycle of operations be performed on a system which at the beginning is in the following condition: One gram of ice at the absolute temperature T is pressed upon with a pressing

[1] The physical interpretation of the negative sign of this pressure obviously is that the pressure is exerted in a direction tending to dilate the liquid. Such pressures as these, which are called negative pressures, have been realized and the behavior of water when subjected to them has been accurately determined by experiment. For a critical summary of our present knowledge of negative pressure in liquids the reader is referred to the previously mentioned article by Professor Hulett.

of P by a piston which is permeable for water-vapor, but not for ice. Separate from this ice is a trace of water which is under the pressing p that is exerted by a piston that is permeable for water-vapor, but not for water. There is free communication for water-vapor throughout the system and its pressure is p'. It is obvious that the pressings P and p must be so selected that it is possible to have the common vapor pressure p' throughout. In such a system the total pressure on the ice is $P + p'$ and on the water $p + p'$.

Fig. 1.

Let the piston on the ice move down and the piston on the water move up until all the ice is evaporated at constant temperature and pressure. During this evaporation and condensation the piston on the ice moves through the volume V_i, the specific volume of ice, and the piston on the water moves through a volume that is slightly less than V_w, the specific volume of water, because the loss of volume resulting from the evaporation of the ice is slightly larger than the gain of volume resulting from the liquefaction of an equal mass of water-vapor. In order therefore to condense all the vapor that is formed from the ice it is necessary to move a piston that exerts the pressure p' on the vapor through the volume $V_i - V_w$. The total work that is obtained from the system during this first portion of the cycle is $pV_w - PV_i - p'(V_i - V_w)$, and the heat which must be supplied to the system in order to keep its temperature constant during the changes is L, the specific heat of fusion of ice.

Let the temperature of the system now sink dT degrees and let either p or P be reduced by an infinitesimal amount. The three pressures now are $p - dp$, $P - dP$, and $p - dp'$. The work that is done in changing these three pressures is so small on account of the very slight compressibility of water and ice that it may be neglected. At this lower temperature $T - dT$ let the pistons move in a manner reverse to that indicated before, thus doing the work $-(p - dp)V_w + (P - dP)V_i + (p' - dp')(V_i - V_w)$, while heat is abstracted from the system to keep its temperature constant. Let the temperature be now raised to its original value T and the pressures on the pistons be changed back to p, P, and p', respectively, the work done in changing then being again neglected.

The cyclic process is now complete, and since it is at every stage

reversible, the second law of thermodynamics requires that the total gain in work divided by the fall in temperature equal the heat absorbed at the higher temperature divided by that temperature; or,

$$(dP/dT)V_i - (dp/dT)V_w + (dp'/dT)(V_i - V_w) = -L/T. \quad (1)$$

With the aid of this general relation let us now calculate the effect on the freezing-temperature of various typical changes of pressure.

4. Calculation of the Changes of Freezing Temperature that Accompany Typical Changes of Pressure.

Case 1. *The total change of pressure on the ice remains equal to the total change of pressure on the water.* In this case $dP + dp' = dp + dp'$, and the general equation (1) becomes $(dP + dp')/dT = -L/T(V_i - V_w)$. This is the well known relation that was shown by James Thomson. In the case of water and ice an increase of pressure of one atmosphere lowers the freezing-temperature 0.00748° C.[1]

Case 2. *The pressing on the water remains constant while the pressing on the ice is changed.* In this case $dp/dT = 0$ and therefore $dP/dT = -L/TV_i - (dp'/dT)(1 - V_w/V_i)$. Since one of the terms on the right of this equation is ten thousand times smaller than the other it can be neglected and the equation written $dP/dT = -L/TV_i$. This is the relation that was first shown by Poynting, and in the case of water it expresses the relation that an increase of pressing of one atmosphere on the ice alone lowers the freezing-temperature 0.0899° C.

Case 3. *The changes of pressing on the ice and the water are so related that the freezing-temperature remains constant.* In this case $dT = 0$, and therefore $(dp + dp')/(dP + dp') = V_i/V_w$. This is the equation that was derived by Lewis, which has been discussed in the introduction to this article.

Case 4. *The pressing on the ice remains constant while the pressing on the water is changed.* In this case $dP/dT = 0$, and therefore $dp/dT = L/TV_w + dp'/dT(V_i/V_w - 1)$; or, neglecting the small

[1] In this calculation and in the succeeding similar ones, the following data are used: latent heat of fusion of ice, 80.1 calories; mechanical equivalent of the calorie, $4.19(10)^7$ ergs; atmospheric pressure, 1,013,200 dynes/cm.^{2}; specific volumes of ice and water at 0°, 1.0909 and 1.0001 cm.^{3} respectively.

term as was done in case two, $dp/dT = L/TV_w$. This coefficient shows that if ice be kept under constant pressing while the pressing on the water is increased one atmosphere the freezing-temperature rises 0.0824°.

It seems to me that this fourth type of freezing, which to my knowledge has not been previously investigated, may occur in the natural freezings of winter weather whenever the conditions that are illustrated by the accompanying figure occur. The closed vessel A is supposed to contain air at atmospheric pressure and to be pierced by an open capillary tube whose lower end is immersed in water W. A piece of ice I is in the vessel and it is obvious that this ice is under the pressing of one atmosphere. Now it has been shown by Lord Kelvin [1] that the vapor-pressure of water which is in a capillary tube is less than that of a plane surface of water; from this fact we may conclude that the system shown in the figure will not be in equilibrium at zero degrees, but that at that temperature the ice will distil over to the water in the capillary tube. The temperature of equilibrium may be calculated as follows: The water in the capillary tube is under a pressing that is less than atmospheric by the hydrostatic pressure of the column of water. If the tube is so small that the capillary rise is (76 × 13.6) centimeters the pressing on the surface in the tube is decreased one atmosphere, and therefore according to the relation shown above the system will be in equilibrium at 0.0824° below zero. If the capillary rise is h centimeters the freezing-temperature is $(h \times 0.0824)/(76 \times 13.6)$ degrees below zero.

Fig. 2.

I wish now to show that this fourth case of freezing is also realized in the freezing of aqueous solutions. The reasoning by which this may be shown has already been given in an elementary form in the introduction to this article. It is obvious that in the freezing of solutions the ice is under atmospheric pressing and that the water is under atmospheric pressing altered by whatever pressing the dissolved substance may exert. If we assume that the dissolved substance exerts the same pressing as a perfect gas, the pressing p is

[1] Proceedings of the Royal Society of Edinburgh, 7, 63 (1870); Maxwell's Heat, 1877, 287.

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given by the relation $p = -cRT$, where R is the gas-constant and c is the concentration of the solution expressed in mols of dissolved substance per liter of solution. If this value of p is substituted in the coefficient of case four, we obtain $dT/dc = -(RT^2V_w)/L$. This expression is identical with the well known relation that Van't Hoff[1] first calculated from the osmotic theory of solution, and which has been repeatedly verified by exact experiments. From the agreement of these two expressions for the molecular depression of the freezing temperature with each other and with experiment we must therefore conclude that the freezing-temperatures of solutions indicate clearly that the solutions are under a negative pressure, comparable with a positive mechanical tension, and that this negative pressure or tension is caused by the dissolved substance and is identical with the osmotic pressure of the solution.

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[1] Lectures on Theoretical and Physical Chemistry. Volume 2.

ON OPTICAL ROTATION.

By Herbert M. Reese.

THE writer was led some time ago to enquire what would be the diffraction-pattern produced by a rectangular opening through which passes a beam of light such that the amplitude is constant over the wave-front, but that the azimuth of the plane of polarization varies continuously and regularly from one side of the opening to the other. These conditions are approximately fulfilled when a beam originally plane-polarized is sent through a prism of some substance such as quartz, which rotates the plane of polarization. The elementary theory of diffraction was applied to this problem, and a result was obtained which seems to be of interest. Throughout the discussion no account was taken of the fact discovered by Fresnel, that in quartz a plane-polarized beam of light is broken up into two circularly-polarized beams, respectively right-handed and left-handed, with different velocities. But it was found in the end that this phenomenon was fully accounted for by the diffraction theory alone, with the simple assumption of rotation; thus showing that Fresnel's phenomenon may be regarded as the consequence of rotation instead of its cause.

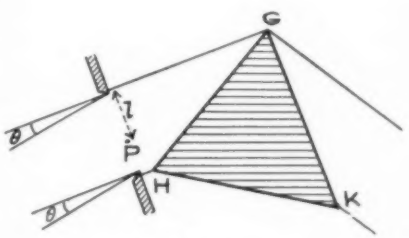

Fig. 1.

Suppose a quartz prism, GHK (Fig. 1), is traversed by a beam of light which emerges from the face, GH, so that the azimuth of the plane of vibration at any point, P, is proportional to the distance, l, from this point to the outer edge of the beam. That is, taking as zero the azimuth at the outer edge,

$$\text{azimuth} = nl.$$

Since transverse waves in mutually perpendicular planes cannot

interfere, in order to determine the diffraction-pattern we must resolve the vibrations into components in two definite azimuths, and then treat each component separately. If we represent by $A \cdot dl$ the amplitude that would be produced in the focal plane by a strip of the wave-front of width dl, its components parallel to and perpendicular to the azimuth o are respectively $A \cos nl \cdot dl$ and $A \sin nl \cdot dl$. For the present we will concern ourselves only with the former.

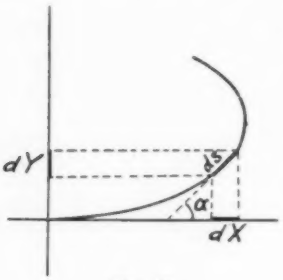

Fig. 2.

Let us find the amplitude of the disturbance produced in the focal plane at an angle θ with the axis of the beam. The phase-difference between the secondary waves coming from P and those coming from the edge of the beam is

$$\frac{2\pi}{\lambda} l \sin \theta = pl,$$

if we let $p = 2\pi/\lambda \sin \theta$. Therefore, if we apply the graphical vector method of Cornu[1] letting ds_x represent the amplitude of the disturbance from P, and α the angle ds_x makes with the X-axis on the vector diagram (*i. e.*, the phase) we have

$$ds_x = A \cos nl \cdot dl,$$

$$\alpha = pl.$$

Therefore:

$$dX_x = A \cos nl \cdot \cos pl \cdot dl,$$

$$dY_x = A \cos nl \cdot \sin pl \cdot dl.$$

The subscript indicates that we are dealing only with vibrations parallel to the azimuth o. To integrate these expressions over the aperture and so find the resultant intensity due to all the vibrations in this direction, we can look upon the vector components X_x and Y_y as respectively the real and the imaginary part of the integral

$$S_x = \int_0^a A e^{ipl} \cos nl \cdot dl,$$

where a is the width of the beam. This gives

$$S_x = \frac{A}{n^2 - p^2}(n \sin na \cdot \cos pa - p \cos na \cdot \sin pa),$$

[1] Preston, The Theory of Light, 3d edition, arts. 45, 147.

$$+\frac{Ai}{n^2-p^2}(n\sin na\sin pa+p\cos na\cos pa-p).$$

Therefore, we have

$$X_x=\frac{A}{n^2-p^2}(n\sin na\cos pa-p\cos na\sin pa),$$

$$Y_x=\frac{A}{n^2-p^2}(n\sin na\sin pa+p\cos na\cos pa-p),$$

and the resultant intensity is

$$I_x=X_x^2+Y_x^2=\frac{A^2}{(n^2-p^2)^2}\{n^2\sin^2 na+p^2\cos^2 na$$
$$+p^2-2p(n\sin na\sin pa+p\cos na\cos pa)\},$$

while the phase of the resultant is given by

$$\tan\Phi_x=\frac{Y_x}{X_x}=\frac{n\sin na\cdot\sin pa+p\cos na\cos pa-p}{n\sin na\cos pa-p\cos na\sin pa}.$$

If we now consider those components of the vibrations which are perpendicular to the azimuth 0 we have

$$ds_y=A\sin nl\cdot dl,$$
$$dX_y=A\sin nl\cdot\cos pl\,dl,$$
$$dY_y=A\sin nl\cdot\sin pl\,dl.$$

These can be integrated by the same process used in the former instance, and we get

$$X_y=\frac{A}{n^2-p^2}(n-n\cos na\cos pa-p\sin na\sin pa),$$

$$Y_y=\frac{A}{n^2-p^2}(p\sin na\cos pa-n\cos na\sin pa),$$

$$I_y=\frac{A^2}{(n^2-p^2)^2}\{n^2+n^2\cos^2 na+p^2\sin^2 na$$
$$-2n(n\cos na\cos pa+p\sin na\sin pa)\},$$

$$\tan\Phi_y=\frac{p\sin na\cos pa-n\cos na\sin pa}{n-n\cos na\cos pa-p\sin na\sin pa}.$$

Therefore the total intensity caused by the two components is

$$I = I_x + I_y = \frac{2A^2}{(n^2 - p^2)^2}\{n^2 + p^2 - 2pn \sin na \sin pa - (n^2 + p^2)\cos na \cos pa\},$$

since I_x and I_y are in mutually perpendicular planes and therefore cannot interfere. Not only is this expression for the whole intensity of the illumination a function of p (and therefore of θ) but the phases Φ_x and Φ_y are also functions of θ, so that it is possible that the light transmitted in any direction θ may be either plane, elliptical or circular in polarization, depending upon the value of θ in terms of a and n. What we are most concerned with is the state of polarization at the maxima of intensity, so that our first step will be to find these maxima.

MAXIMA AND MINIMA.

A casual examination of the general formula, which can be put in the form

$$I = \frac{2A^2}{(n^2 - p^2)^2}\{(n^2 + p^2)(1 - \cos na \cos pa) - 2pn \sin na \sin pa\},$$

reveals the interesting fact that the center of the field is not necessarily a maximum. If we put $\theta = 0$ and, therefore, $p = 0$, we get

$$I = \frac{2A^2}{n^2}(1 - \cos na),$$

and if the width of the beam happens to be such that $\cos na = 1$ (a perfectly possible case) this reduces to 0. This shows that the center of the field may even be dark, and it will be shown later that it is in general either a minimum or a secondary maximum, unless the width of the beam is small.

The general condition for a maximum or a minimum is that $dI/dp = 0$,

$$\frac{dI}{dp} = \frac{2A^2}{(n^2 - p^2)^3}\{2p(3n^2 + p^2)(1 - \cos na \cos pa) + a(n^4 - p^4)\cos na \sin pa - 2n(3p^2 + n^2)\sin na \sin pa - 2pna(n^2 - p^2)\sin na \cos pa\} = 2A^2 \frac{\varphi(p)}{(n^2 - p^2)^3}.$$

The numerator $\varphi(p)$ vanishes for $p = 0$, $p = n$, and other values. The denominator also vanishes for $p = n$. To find the value of the fraction for this indeterminate case we must make successive differentiations. The first and second derivatives of the denominator vanish when $p = n$, the third reduces to $-48n^3$. The first and second derivatives of the numerator vanish when $p = n$, while the third reduces to

$$12 \sin^2 na - (12\, na + 8n^3a^3) \sin na \cos na.$$

Therefore $p = n$ gives a maximum or a minimum if $\sin na = 0$ or if

$$\tan na = \frac{na(3 + 2n^2a^2)}{3},$$

but not otherwise. Owing to the symmetry of the expression for I, if there is a maximum or a minimum when $p = p_1$, the same will occur when $p = -p_1$.

It will now be shown, however, that in any case if a is large there is a maximum or a minimum near $p = n$. Let us find the condition that a maximum or a minimum is given by $p = n + \epsilon$, where ϵ is some small quantity. We can express $\varphi(n + \epsilon)$ in the following series form:

$$\varphi(n+\epsilon) = \varphi(n) + \epsilon \frac{d\varphi(n)}{dp} + \frac{\epsilon^2}{2}\frac{d^2\varphi(n)}{dp^2} + \frac{\epsilon^3}{3!}\frac{d^3\varphi(n)}{dp^3} + \frac{\epsilon^4}{4!}\frac{d^4\varphi(n)}{dp^4} + \cdots$$

$$= \frac{\epsilon^3}{3!}\frac{d^3\varphi(n)}{dp^3} + \frac{\epsilon^4}{4!}\frac{d^4\varphi(n)}{dp^4} + \cdots,$$

since, as we have just seen, $\varphi(n)$ and its first two derivatives vanish. Therefore we have

$$\frac{\varphi(n+\epsilon)}{[n^2 - (n-\epsilon)^2]^3} = \frac{-1}{\epsilon^3(2n+\epsilon)^3}\left\{\frac{\epsilon^3}{3!}\frac{d^3\varphi(n)}{dp^3} + \frac{\epsilon^4}{4!}\frac{d^4\varphi(n)}{dp^4} + \cdots\right\}.$$

The condition that the first two terms vanish is

$$\epsilon = -4\frac{d^3\varphi(n)}{dp^3} \div \frac{d^4\varphi(n)}{dp^4},$$

$$\frac{d^3\varphi(n)}{dp^3} = 12 \sin^2 na - (12na + 8n^3a^3) \sin na \cos na.$$

$$\frac{d^4\varphi(n)}{dp^4} = 24a \cos na \sin na + 24na^2 (\sin^2 na - \cos^2 na) + 8n^3a^4.$$

Therefore, the condition is

$$\epsilon = \frac{-12 \sin^2 na + (12na + 8n^3a^3) \sin na \cos na}{32a \{3 \cos na \sin na + 3na (\sin^2 na - \cos^2 na) + n^3a^3\}}.$$

Therefore, if a is large, a small value of ϵ can be found which will make $\varphi(n+\epsilon)/(n^2-p^2)^3$ depend upon terms of the order $\epsilon^2/8n^3$, so that a maximum or a minimum occurs near $p = \pm n$.

Fig. 3 is drawn to scale so as to show the relation between I and

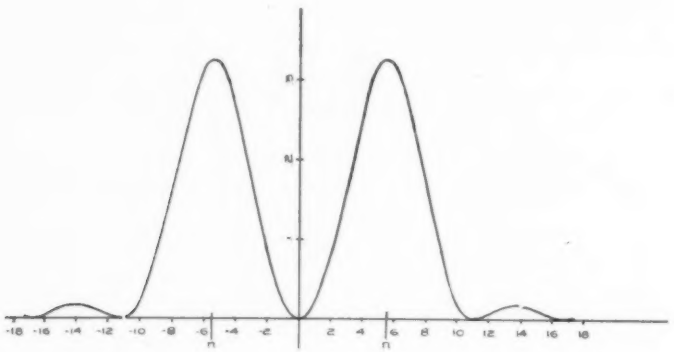

Fig. 3.

p where n has the value 5.52 (about the value for an actual quartz prism belonging to the University of Missouri) and $na = 2\pi$. Fig. 4 shows the same thing where $na = 7\pi/2$. Curves have been plotted for a number of other cases; and in every case except for unusually small values of na (less than π) the intensity at the middle of the field is zero or very small, a large maximum occurs where $p = \pm n$ or near there, and there are several small maxima. Hence the general effect is to produce a double line in the focal plane. The polarization of this doublet will be considered later.

Hereafter we will confine our attention to the case where $\sin na = 0$ and $\cos na = 1$. In this case the general formula for I becomes much simpler and can be handled more easily. Moreover we have seen that under such circumstances a maximum or a minimum is given by $p = n$; and we know from physical considerations that

any such conclusions drawn for this case will apply approximately to any other, provided na be large. For, suppose $na = 2\pi k$, where k is a large integer, then the additional width of beam necessary to make $na = 2\pi(k + \epsilon)$, where ϵ is any number between 0 and 1, will

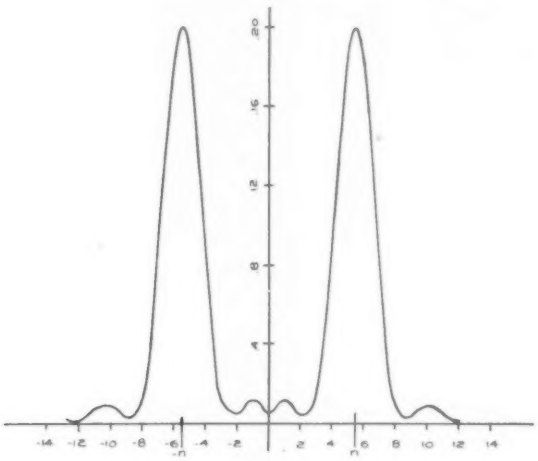

Fig. 4.

be small compared to the original width, and therefore will not seriously affect the diffraction pattern.

If we put $\sin na = 0$ and $\cos na = 1$, the general formula becomes

$$I = \frac{2A^2}{(n^2 - p^2)^2}(n^2 + p^2)(1 - \cos pa),$$

and the condition for a maximum or a minimum is

$$\frac{1}{(n^2 - p^2)^3}\{2p(3n^2 + p^2)(1 - \cos pa) + (an^4 - ap^4)\sin pa\} = 0.$$

We have seen that this vanishes when $p = n$. To determine whether it is a maximum or a minimum, we take the second derivative :

$$\frac{1}{2A^2}\frac{d^2I}{dp^2} = \frac{1}{(n^2 - p^2)^4}\{(6n^4 + 36n^2p^2 + 6p^4)(1 - \cos pa)$$

$$+ (12apn^4 - 8ap^3n^2 - 4ap^5)\sin pa$$

$$+ (a^2n^6 - a^2n^4p^2 - a^2n^2p^4 + a^2p^6)\cos pa\} = \frac{M}{Q}.$$

Both M and Q and their first three derivatives vanish when $p = n$; but

$$\frac{d^4M}{dp^4} = -16n^2a^2(n^2a^2 - 1),$$

$$\frac{d^4Q}{pd^4} = 384n^4$$

Therefore

$$\frac{1}{2A^2}\frac{d^2I}{dp^2} = -\frac{16n^2a^2(n^2a^2 - 1)}{384n^4} = -\frac{a^2}{24n^2}(a^2n^2 - 1).$$

Since $na = 2\pi k$, where k is a positive integer, d^2I/dp^2 is negative. Therefore I is a maximum. Hence, since the two principal maxima occur at $p_1 = n$ and $p_2 = -n$, their angular separation is given by

$$p_1 - p_2 = \frac{2\pi}{\lambda}\sin\theta_1 - \frac{2\pi}{\lambda}\sin\theta_2 = 2n,$$

or, approximately,

$$\theta_1 - \theta_2 = \frac{n\lambda}{\pi}.$$

POLARIZATION AT THE PRINCIPAL MAXIMA.

If, in the expressions for Φ_x and Φ_y, we put $\sin na = 0$ and $\cos na = 1$ we get for the phases of the two mutually perpendicular components of the vibrations

$$\tan\Phi_x = \frac{1 - \cos pa}{\sin pa},$$

$$\tan\Phi_y = \frac{-\sin pa}{1 - \cos pa}.$$

From the form of these expressions it is evident that Φ_x, Φ_y, and therefore $\Phi_x - \Phi_y$ have opposite signs on the two sides of the center of the field (*i. e.*, changing the sign of p changes the sign of each). If we put $p = n$, remembering that $\sin na = 0$, $\cos na = 1$, these take indeterminate forms which reduce to

$$\tan\Phi_x = 0 \qquad \text{or} \quad \Phi_x = 0 \text{ or } \pi,$$

$$\tan\Phi_y = -\infty \quad \text{or} \quad \Phi_y = \pm\frac{\pi}{2}.$$

If we put $p = -n$,

$$\tan \Phi_x = 0 \qquad \text{or} \quad \Phi_x = 0 \text{ or } \pi,$$

$$\tan \Phi_y = -\infty \quad \text{or} \quad \Phi_y = \pm \frac{\pi}{2}.$$

Therefore, since for the two values $p = n$ and $p = -n$ the phase-difference is equal to $\pi/2$ in each case but of opposite signs, the angles corresponding to these values will give directions along which the transmitted light is circularly polarized in opposite senses, provided only that I_x and I_y are equal in each case. This is easily seen to be true from the original formulæ, for

$$I_x = \frac{2A^2}{(n^2 - p^2)^2}(p^2 - p^2 \cos pa),$$

$$I_y = \frac{2A^2}{(n^2 - p^2)^2}(n^2 - n^2 \cos pa).$$

And these become identical when $p = \pm n$, and although each becomes indeterminate in form, each reduces to the value $A^2a^2/2$.

We have thus arrived at an explanation of the phenomenon observed by Fresnel without making any assumption as to the velocity of circularly polarized light in the prism. However, it will be shown later that the mere fact of rotation is a proof that the apparent velocities of right-handed and of left-handed circularly-polarized light are different in the rotating medium; and therefore the explanation by Fresnel and that given here are equivalent.

In order to see whether the angular separation predicted by the above theory is the same as that required in Fresnel's theory, it is necessary to express the latter in terms of the quantity n.

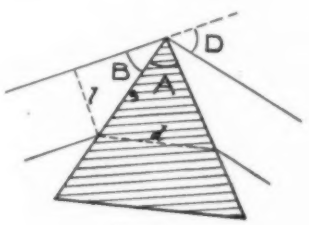

Fig. 5.

In Fig. 5,

$$l = s \sin B,$$

$$d = 2s \sin \tfrac{1}{2}A.$$

If v and $v + dv$ represent the velocities of the two rays in quartz and λ' the wave-length in quartz, then the phase-difference between the two rays on emerging is

$2\pi/\lambda' v\, dv$. Therefore, the rotation, which is half the phase-difference is

$$\varphi = \frac{\pi d}{\lambda' v} dv.$$

We have defined n as φ/l, therefore,

$$n = \frac{\pi d}{\lambda' v l} dv = \frac{2\pi}{\lambda'} \frac{dv}{v} \frac{\sin \frac{1}{2}A}{\sin B}.$$

But $A + 2B = 180° - D$, therefore,

$$n = \frac{2\pi}{\lambda'} \frac{dv}{v} \cdot \frac{\sin \frac{1}{2}A}{\cos \frac{1}{2}(A + D)}.$$

From the formula for the refractive index, we have

$$\frac{v_0}{v} = \frac{\sin \frac{1}{2}(A + D)}{\sin \frac{1}{2}A},$$

where v_0 is the velocity in air. Therefore,

$$\frac{dv}{v} = -\frac{v}{2v_0} \frac{\cos \frac{1}{2}(A + D)}{\sin \frac{1}{2}A} \cdot dD.$$

Substituting this we get

$$n = -\frac{\pi}{\lambda'} \frac{v}{v_0} dD.$$

Since $\lambda' v_0/v = \lambda$, the wave-length in air, we have

$$n = -\frac{\pi}{\lambda} \cdot dD,$$

$$dD = \theta_1 - \theta_2 = -\frac{\lambda n}{\pi}.$$

This is the same angular separation as that given above by the diffraction theory, the difference in sign being of no consequence.

CIRCULARLY-POLARIZED LIGHT.

Suppose the light entering the prism, instead of being plane, were circularly-polarized, say in the right-handed sense. To find the form of the diffraction pattern we must suppose the vibrations broken up into two mutually perpendicular ones with a phase-dif-

ference of $\pi/2$, and treat each separately. We will as before confine our attention to the special case where $\sin na = 0$ and $\cos na = 1$. Each of the parts into which we have divided the incident light will produce in the focal plane two mutually perpendicular components of the types I_x and I_y. The I_x due to the second part of the incident beam will be parallel to the I_y of the first part and in the same direction, while the I_y of the second part will be parallel to the I_x of the first part but in the *opposite* direction. Let I_x', I_y', X_x', Y_x', X_y', Y_y', etc., refer to the first part of the incident beam, I_x'', I_y'', X_x'', etc., to the second part. Then we have, since I_y'' is opposite in direction to I_x',

$$X_x' = -\frac{Ap}{n^2 - p^2}\sin pa, \qquad X_y' = \frac{An}{n^2 - p^2}(1 - \cos pa),$$

$$Y_x' = -\frac{Ap}{n^2 - p^2}(1 - \cos pa), \qquad Y_y' = \frac{-An}{n^2 - p^2}\sin pa,$$

$$X_x'' = \frac{-Ap}{n^2 - p^2}\sin pa, \qquad X_y'' = \frac{-An}{n^2 - p^2}(1 - \cos pa),$$

$$Y_x'' = -\frac{Ap}{n^2 - p^2}(1 - \cos pa), \qquad Y_y'' = \frac{An}{n^2 - p^2}\sin pa.$$

Since there is a phase-difference of $\pi/2$ between I_x' and I_y'', I_y' and I_y'', we have for the resultant components on the vector diagram,

$$X_x = X_x' - Y_y'' = \frac{A \sin pa}{p - n},$$

$$Y_x = Y_x' + X_y'' = \frac{A(1 - \cos pa)}{p - n},$$

$$X_y = X'_y - Y_x'' = -\frac{A(1 - \cos pa)}{p - n},$$

$$Y_y = Y_y' + X_y'' = \frac{A \sin pa}{p - n}.$$

Let us substitute in these formulæ the value $p = n$. All become indeterminate in form but reduce to the following :

$$X_x = \frac{Aa \cos pa}{1} = Aa,$$

$$Y_x = \frac{Aa \sin pa}{1} = 0,$$

$$X_y = -\frac{Aa \sin pa}{1} = 0,$$

$$Y_y = \frac{Aa \cos pa}{1} = Aa.$$

This indicates a simple circularly-polarized beam. On the other hand, if we put $p = -n$ we get

$$X_x = Y_x = X_y = Y_y = 0.$$

Therefore, if circularly-polarized light passes into the prism, one member of the usual doublet in the focal plane is missing, and the other is circularly polarized, like the incident light. Hence we may say that circularly-polarized light passes through the prism unaltered, the deviation being different for right-handed and for left-handed beams.

It is not to be understood that this theory is offered as a substitute for that of Fresnel, or that the claim is made that it is simpler or preferable in any way. Its aim is to show that instead of regarding the rotation of the plane of polarization as a consequence of the fact that right-handed and left-handed beams travel with different velocities, we may just as truly regard the latter fact as a consequence of the former. Fresnel's so-called explanation of rotation is not really a relation between cause and effect, but merely a mathematical point of view, and the point of view presented in this paper is just as good.

It has been shown by H. T. Eddy[1] that a difference between the velocities follows as a consequence of the rotatory power of the medium, by methods entirely different from those used here. It is not necessary, however, to use analytic methods to prove this, as the following purely geometrical considerations will show. Suppose

[1] PHYS. REV., XX., April, 1905.

we have a parallel-sided plate of a material with right-handed rotatory power, and incident upon it a right-handed circularly-polarized beam. Suppose the beam to be analyzed into two plane-polarized beams in planes at right-angles, with a phase-difference of $\pi/2$. Each of these in passing through the plate will have its plane rotated by a certain amount. Suppose the thickness of the plate to be such that it contains n wave-lengths of the plane-polarized beams. On emerging from the plate the two beams can be regarded as again producing circularly-polarized light, but owing to the rotation which each has experienced the new beam will have suffered an advance in phase which is equivalent to a shortening of the wave-length, as if there were now more than n waves in the thickness of the plate. This again is equivalent to a decrease in velocity. On the other hand, if the incident light had been left-handed, there would have been an apparent increase in wave-length and in velocity. Hence, if the velocity be measured by any interferential method, or by any other means depending upon the wave-length, we will obtain a different velocity for the two kinds of light. However, there is no reason at all to suppose that, if the velocity were measured by the fundamental method of the rotating mirror or the toothed wheel, any difference would be observed; on the other hand it is hard to conceive how, measured in this way, the velocity of a circularly polarized ray should be any different from that of the plane-polarized rays to which it is equivalent. We may say that there is a difference in the wave velocity, but not in the group velocity. It seems to the writer that this distinction is rather important. One can form a mental picture of this condition by imagining a long rotating corkscrew. The apparent wave-motion has a certain velocity, but a point moving along the screw and following its convolutions (which point can represent the van of a train of waves) might have a velocity in the direction of the waves greater or less than this.

Of course it is needless to point out that whatever results have been arrived at in this paper apply equally well to any other optically rotating medium as well as quartz, whether this rotating power be a natural quality of the material or be induced by magnetic effects.

A summary of the points brought out is here presented:

1. The separation of a plane-polarized beam into two circularly-polarized beams with different deviation is explained by the theory of diffraction alone.

2. The difference in the apparent velocity of right-handed and left-handed circularly-polarized waves is also accounted for by the same theory.

3. This difference only applies to the velocities as measured by interference methods. The group velocity, or the velocity of the front of a train of waves, is independent of the polarization.

4. This theory is mathematically equivalent to that of Fresnel, the two being merely the result of different points of view.

UNIVERSITY OF MISSOURI,
January 2, 1906.

STUDIES IN LUMINESCENCE.

VI. The Decay of Phosphorescence in Sidot Blende.[1]

By Edw. L. Nichols and Ernest Merritt.

THE decay of phosphorescence was first studied by E. Becquerel.[2] In the case of short-duration phosphorescence the phosphoroscope was used for this purpose and the intensity of phosphorescence was measured for different speeds of the rotating disc. Becquerel regarded it as probable that the law of decay was of the form

$$I = I_0 \epsilon^{-at}, \tag{1}$$

and found that the observations were in fact fairly well represented by an exponential expression. In discussing these observations, however, Becquerel tacitly assumed that no appreciable time was required for the exciting rays to produce their full effect. Later investigations have shown that this assumption is not justified. Since a change in the speed of the phosphoroscope altered not only the time that elapsed between excitation and observation, but also the duration of exposure, it is probable, therefore, that the initial excitation was less at high speeds. Attention was directed to this point by E. Wiedemann and later by H. Becquerel, who states that a recomputation of the data shows a less satisfactory agreement with the exponental law than at first appeared.

For the long-time phosphorescence of the phosphorescent sulphides E. Becquerel proposed an empirical expression of the form

$$I^m(c + t) = cI_0^m. \tag{2}$$

For each of the seven substances tested this expression was found to show a fairly good agreement with the experimental results

[1] An account of the work described in this paper was presented to the American Physical Society at the meeting held on Oct. 28, 1905. An abstract appeared in the Physical Review, Vol. XXI., p. 411, December, 1905.

[2] Becquerel, "La Lumière." See also Comptes Rendus, Vol. 51, p. 921, 1860, and Annales de Chimie et de Physique, Series 4, Vol. 62, p. 5.

throughout a considerable range. In one case, namely that of a calcium sulphide preparation giving an orange-red phosphorescence, the expression represented the observations with considerable accuracy throughout the whole range, the value of m being 0.5. But in most cases it was not possible to find values of m and c which would make the formula fit the experimental data for the whole time of decay. The values of m that suited the observations best lay between 0.5, for the calcium sulphide just mentioned, and 0.806 for another calcium sulphide having an orange yellow phosphorescence.

The same empirical formula has since been very generally used; among others by Darwin[1] in 1881, and Ch. Henry[2] in 1892. The former worked with Balmain's paint and found the best value for m to be 0.86. It cannot be said, however, that the experimental results were represented very accurately by the formula. The substance used by Henry was Sidot's blende, several different samples of which were tested. Henry states that in the case of one specimen the results were represented by an exponential law (eq. 1) for 14 seconds, while other preparations obeyed the law

$$i^{0.5936}(t + 27.18) = 1{,}647.5 \qquad (3)$$

Henry appears to have been convinced of the corrections of the latter law and proposed a new type of photometer which made use of the gradually decaying phosphorescence of Sidot blende in the measurement of faint sources of light.[3] While the fact that the constant in eq. (3) is given to five significant figures indicates an accuracy that is unusual in photometric measurements, the lack of experimental data in the paper referred to makes it difficult to form an independent opinion of the significance of the conclusions.

The decay of phosphorescence was considered from the theoretical standpoint by H. Becquerel[4] in 1891. Upon the assumption that the light emitted during phosphorescence was due to molecular vibrations set up by the action of the exciting light and afterwards gradually dying out, it was shown that the law of decay would be

[1] Philosophical Magazine, Vol. 11, p. 209, 1881.
[2] Comptes Rendus, Vol. 115, p. 505, 1892.
[3] Comptes Rendus, Vol. 115, p. 602.
[4] Comptes Rendus, Vol. 113, p. 618, 1891.

determined by the nature of the damping forces. If the vibrations meet with an opposing force proportioned to the speed it was shown that an exponential law of decadence would result; while if the resistance is proportional to the square of the speed the law of decadence would take the form

$$I = \frac{1}{(a + bt)^2}. \tag{4}$$

It will be noticed that the emprical law proposed by E. Becquerel reduces to (4) in case $m = 0.5$.

In the case of a substance whose phosphorescent spectrum contains several bands Becquerel proposed the expression

$$I = \Sigma \frac{1}{(a + bt)^2}, \tag{5}$$

in which there is one term in the summation for each band. Upon testing this law with the data obtained by E. Becquerel for a calcium sulphide giving blue phosphorescence it was found that the results could be expressed by the use of two terms in the above series with great accuracy. The existence in the spectrum of this substance of two bands possessing independent properties could be demonstrated in various ways.

In the derivation of the law proposed by H. Becquerel the assumption is that the vibrations set up by the action of the exciting light continue during several minutes or even hours. This would imply either that the vibrating atoms or molecules exist during this time without collisions with other molecules, or else that such collisions are without effect upon the vibrations. Neither of these suppositions seems to us tenable. But the law nevertheless appears to be of very general application. We shall show later that the same law may be derived from entirely different theoretical considerations.

In all of the experiments upon the decay of phosphorescence with which we are familiar it is the total light that has been measured; so far as we are aware no attempt has been made to determine the law of decay for different portions of the phosphorescence spectrum. This fact complicates the problem greatly, for in most

cases of phosphorescence the spectrum consists of two or more bands, which, in general, decay at different rates. It can hardly be expected, therefore, that measurements of the total light will be found to obey a simple law. The difficulties resulting from the complexity of the luminescence spectrum were recognized by E. Becquerel and were several times mentioned in the course of his classic researches. In discussing his experiments on decadence he suggested an expression of the form

$$I = Ae^{-at} + Be^{-\beta t} + \cdots \qquad (6)$$

for the intensity of the total phosphorescence, with one term for each band in the spectrum. But the difficulties of computation were such as to lead him to abandon this expression and to employ instead the empirical expression of eq. (2). Recognition of the fact that each band has its own rate of decay is also implied in the law proposed by H. Becquerel (eq. 4).

EXPERIMENTAL.

While it is possible to test the corrections an expression of the form of (4) or (6) by comparison with measurements of total intensity, such a test is difficult, and cannot be altogether satisfactory; for with an expression containing several terms the number of constants is so great that the law may be made to fit almost any data. It is clear that a much more severe test of any given law of decay may be obtained from experiments with a substance having only one band in its phosphorescence spectrum. The Sidot blende screen used by us in earlier experiments[1] was found to have three bands in its luminescence spectrum. But since the two violet bands do not appreciably overlap the green band the spectrophotometer enables the behavior of the latter band alone to be conveniently studied. The matter is still further simplified by using the violet rays of the arc in excitation, since these rays, while they produce a brilliant green luminescence, are incapable of exciting either one of the violet bands.[1] In view of the brilliancy of the green band, its long duration, and the ease in which it may be isolated, this band seems well adapted to the study of the decay of phosphorescence.

Our previous experiments on Sidot blende have shown that in the case of the green band the phosphorescence spectrum shows no

[1] PHYSICAL REVIEW, Vol. XXI., p. 247, 1905.

measurable change in form during the first ten seconds of decay. In other words, the rate of decay is the same for all wave-lengths. To fix the behavior of the whole band it would be sufficient, therefore, to determine the law for a single wave-length. We have, however, made measurements at three different wave lengths, namely, at 0.483 μ, 0.512 μ and 0.547 μ. The first of these wave-lengths lies near the ultra edge of the band; the second is not far from the maximum; and the third is near the red edge.

The methods of measurement were the same as those described in our last paper.[1] The experimental data obtained are contained

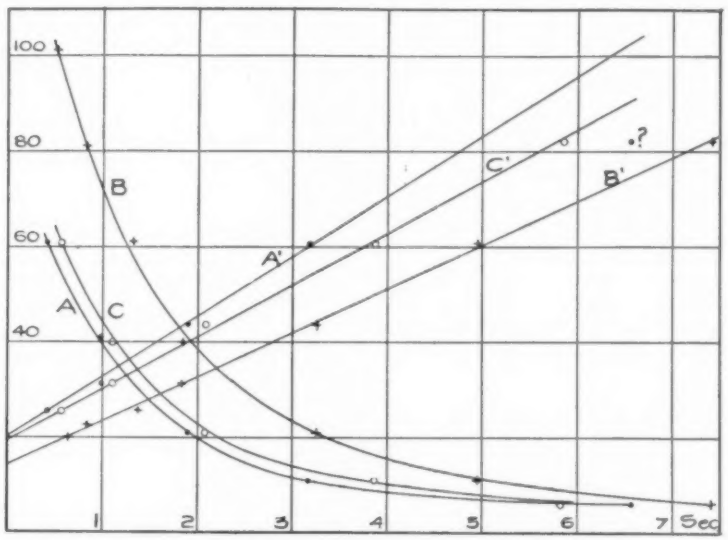

Fig. 36. Curves A, B and C show the decay in the phosphorescence of Sidot blende for the wave-length 0.483 μ, 0.512 μ and 0.547 μ, respectively. The curves A', B' and C' are obtained from A, B and C by plotting $I^{-\frac{1}{2}}$ instead of the intensity of phosphorescence, I.

in the following three tables. In each case it is the average of from ten to twenty observations that is recorded.

In the set of observations contained in Table I. the curves for 0.547 μ, 0.483 μ and 0.512 μ were determined during the forenoon in the order just stated. The data for 0.512 μ with weaker excitation were observed during the afternoon of the same day.

[1] PHYSICAL REVIEW, Vol. XXI., p. 247, 1905.

The observations recorded in Table II. were taken in a different manner, the measurements at a given intensity being made for each of the three wave-lengths in succession. The observations of December 13 (Table III.) were made in a similar manner. The first three curves of Table I. are plotted in Fig. 36, while the second and fourth curves of this table are shown in Fig. 37.

TABLE I. [NOV. 25.]

Time in Seconds Required for the Phosphorescence to Fall from its Initial Intensity to the Intensity I. The Computed Values of t are Derived by Substitution in the Following Equations:

For $\lambda = 0.483\,\mu$ $1/\sqrt{I} = 0.102 + 0.059\,t$
$\lambda = 0.512\,\mu$ $1/\sqrt{I} = 0.074 + 0.045\,t$
$\lambda = 0.547\,\mu$ $1/\sqrt{I} = 0.096 + 0.055\,t$
$\lambda = 0.512\,\mu$ (weaker excitation) $1/\sqrt{I} = 0.092 + 0.052\,t$

I	$\lambda = 0.483\,\mu$		$\lambda = 0.512\,\mu$		$\lambda = 0.547\,\mu$		$\lambda = 0.512\,\mu$ Weaker Excitation.	
	t sec. Obs.	t sec. Comp.	t sec. Obs.	t sec. Comp.	t sec. Obs.	t sec. Comp.	t sec. Obs.	t sec. Comp.
101			0.63	0.58				
81			0.83	0.85				
61	0.41	0.44	1.38	1.20	0.56	0.58	0.72	0.69
41	0.99	0.92	1.84	1.83	1.10	1.09	1.24	1.23
21	1.88	1.98	3.25	3.23	2.07	2.23	2.42	2.45
11	3.16	3.39	4.95	5.10	3.87	3.74	4.03	4.04
6	6.55	5.23	7.42	7.50	5.82	5.71	6.22	6.92

TABLE II. [DEC. 10.]

Time in Seconds Required for the Phosphorescence to Fall to the Intensity I. The Computed Values of t are Derived by Substitution in the Following Equations:

For $\lambda = 0.512\,\mu$ $1/\sqrt{I} = 0.078 + 0.034\,t$ $\lambda = 0.547\,\mu$ $1/\sqrt{I} = 0.104 + 0.042\,t$

I	$\lambda = 0.483\,\mu$		$\lambda = 0.512\,\mu$		$\lambda = 0.547\,\mu$	
	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.
81.4	0.60		1.06	0.98	0.30	0.22
61.4	0.77		1.35	1.49	0.55	0.62
31.4	2.40		2.98	3.02	1.83	1.84
11.4	4.13		6.47	6.46	4.62	4.58

TABLE III. [DEC. 13.]

Time in Seconds Required for the Phosphorescence to Fall to the Intensity I. The Computed Values of t are Derived by Substitution in the Following Equations:

For $\lambda = 0.483\ \mu$ $1/\sqrt{I} = 0.104 + 0.070\ t$
$\lambda = 0.512\ \mu$ $1/\sqrt{I} = 0.094 + 0.046\ t$ $\lambda = 0.547\ \mu$ $1/\sqrt{I} = 0.118 + 0.070\ t$

I	$\lambda = 0.483\ \mu$		$\lambda = 0.512\ \mu$		$\lambda = 0.547\ \mu$	
	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.
81.4			0.45	0.37		
61.4	0.45	0.36	0.69	0.74	0.25	0.14
31.4	1.06	1.08			0.88	0.87
21.4	1.46	1.61	2.60	2.67	1.30	1.40
11.4	2.78	2.76	4.48	4.44	2.61	2.55
7.4	4.46	3.80	5.97	6.00	4.58	3.57

The data of the preceding tables have been used to test the applicability of each of the several proposed laws of decay to the case of a single band. It was found that the results can be closely represented by an expression of the form given in eq. (4). To determine the constants a and b of this equation a convenient graphical method was employed, in which the values of $1/\sqrt{I}$ were plotted as ordinates and times as abscissas. Since eq. (4) may be written in the form

$$\frac{1}{\sqrt{I}} = a + bt,$$

the points located in this manner should lie on a straight line. A straight line having been drawn as nearly as possible through all the points, the slant of this line and its y intercept at once gave the values of b and a respectively. The values of a and b determined in this way are given in each of the tables, and the values of t computed from the above equation are tabulated for comparison with the times observed.

In Figs. 36 and 37 the values of $I^{-\frac{1}{2}}$ have been plotted as described above. It will be noticed that in each case the points lie very nearly upon a straight line, and that there is nothing to indicate any systematic variation from linearity. In the case of one curve, namely that for 0.483 μ in Table II., the points located in this

way did not lie even approximately on a straight line. This curve, therefore, does not have the form corresponding to eq. (4). But in the case of the other curves, including one taken at this same wave-length (Table I.), the agreement between the observed and computed values of t is satisfactory, the differences being only such as might well result from accidental errors. It seems probable therefore that the observations at 0.483 μ in Table II. were subject to some unusual source of error.

In Fig. 36 it will be noticed that one point of the line A' (indi-

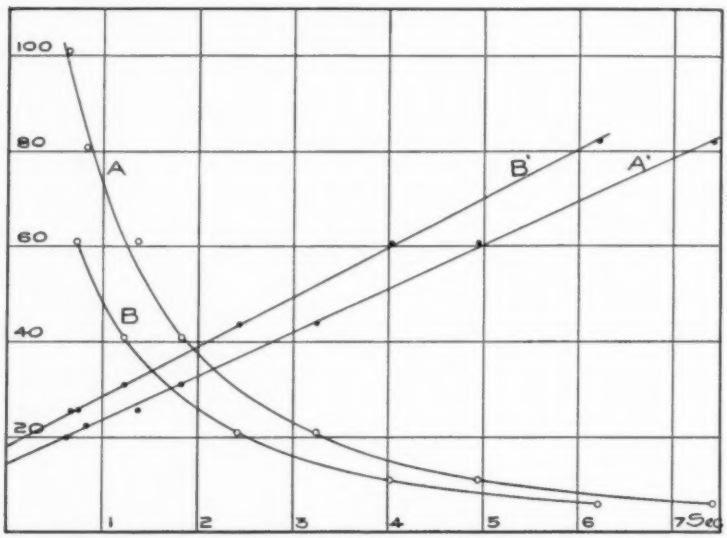

Fig. 37. Curves A and B show the decay of phosphorescence at 0.512 μ for two different intensities of the exciting light. In the curves A' and B' $I^{-\frac{1}{4}}$ is plotted instead of the intensity I.

cated by a question mark) falls below the line, *i. e.*, the observed time of decay was considerably greater than that computed from an assumed linear relation between $I^{-\frac{1}{4}}$ and t. Discrepancies of the same kind will be found for the smallest values of I in the first curve of Table I. and for the first and last curves of Table III. No such discrepancies are present in any of the four curves taken at 0.512 μ — *i. e.*, near the maximum of the phosphorescence spectrum. If these cases of disagreement between the observed and computed values of t are not due to accidental errors,

they show that the violet edge of the phosphorescence band dies out more gradually than the maximum. Our previous observations[1] had indicated that if any difference exists between the two rates, the violet end of the band decays more rapidly than the center. Because of these conflicting indications, and especially because of the difficulties of making accurate readings for small intensities, we are inclined to ascribe the seeming variations from linearity to accidental errors.

THEORETICAL.

In attempting to interpret the results of the foregoing experiments we have found it useful to consider the subject from the standpoint of a hypothesis first proposed in explanation of luminescence phenomena by E. Wiedemann[2] and later modified and extended by Wiedemann and Schmidt.[3] According to this view some chemical or physical change is produced in a luminescent substance during excitation, and the emission of light is an accompaniment of the more or less gradual restoration of the modified substance to its original condition. Thus, in the case of phosphorescence, it was suggested by Wiedemann that a portion of the active material was changed by the exciting light from the stable condition *A* into the unstable state *B*. Phosphorescence would then result from a gradual breaking down of the unstable compound.[4] Wiedemann pointed out that this hypothesis leads to an exponential law of decay.[5]

While the change called for by the theory here considered has usually been assumed to be of a chemical nature, it was pointed out

[1] PHYSICAL REVIEW, Vol. XXI., p. 257.

[2] E. Wiedemann, Zur Mechanik des Leuchtens. Wied. Ann., Vol. 37, p. 177, 1889.

[3] E. Wiedemann und G. C. Schmidt. Wied. Ann., Vol. 56, p. 177, 1895.

[4] "Das auffallende Licht ruft chemische Modificationen in den phosphorescierenden Körpern hervor, die nachher wieder im umgekehrten Sinne durchlaufen werden und dabei eine Lichtentwickelung hervor rufen. . . . In Bezug auf die chemische Veränderungen dürfte die Anschauung wahrscheinlich sein, dass das Schwefelcalcium etc. in zwei Modificationen, einer stabilen und einer labilen *A* und *B*, bestehen kann. Die Modification *A* wird durch Absorption gewisser Strahlen in die Modification *B* verwandelt, welche allmählich unter Lichtentwickelung sich in *A* zurück verwandelt. . . . Da die Substanzen schon während der Belichtung phosphorescieren, so muss die Rückbildung auch während derselben vor sich gehen." E. Wiedemann, l. c., p. 224–5.

[5] Wiedemann, l. c., p. 226.

by Wiedemann and Schmidt[1] that in many cases there were reasons for looking upon electrolytic dissociation as the more probable cause of luminescence. The increased conductivity of fluorescent solutions during fluorescence[2] adds support to this view. But although it is probable that the exciting light causes a separation of the active molecule into positive and negative parts, it appears to us unlikely that these parts are the ions of ordinary electrolysis. There are many substances like fluorescein and eosin which fluoresce only when dissociated. In such cases fluorescence cannot be due to the recombination of ions; for dissociation and recombination are taking place in an electrolytic solution all the time, and if this were the cause of luminescence we should expect the solution to glow continuously without the action of any exciting light. Fluorescence in such cases must be due to some action of the exciting light upon one of the ions. We have suggested elsewhere that this action may be a dissociation similar to that produced in gases by the Roentgen rays.

Assuming the correctness of the Wiedemann hypothesis in its general features it seems clear that dissociation in the case of photo-luminescence is a result of the violent vibrations set up in the molecules of the active substance by the exciting light. A certain number of the active molecules are actually torn apart, and the resulting negative electrons and positive nuclei exist for a time uninfluenced by their mutual attraction. The vibrations that occur upon the recombination of the ions give rise to luminescence. This view at once explains the well known fact that the light from an isotropic luminescent body is unpolarized, whatever may be the state of polarization of the exciting light.[3]

The fact that the light emitted during luminescence is of different wave-length from the exciting light seems at first to speak against the above explanation of photo-luminescence. Why should the vibrations that occur on recombination differ in period from those originally set up by the exciting light? It is indeed possible that the latter are forced vibrations, whose period bears no simple rela-

[1] L. c., pp. 244–247.

[2] Nichols & Merritt, PHYSICAL REVIEW, Vol. 19, p. 396, 1904.

[3] Seeming exceptions to this statement probably result from polarization by emission. See Millikan, PHYSICAL REVIEW, Vol. 3, p. 97.

tion to the natural period of the molecule. But it is more reasonable to expect that vibrations which bring about actual disintegration are produced by resonance. If this is true we have to do with the natural period of the molecule in both cases, and it would seem that the light emitted during luminescence should have the same wave-length as the exciting light. In the discussion that follows we venture to make a suggestion which offers an explanation of this difficulty.

In the case of photo-luminescence in solids and liquids the active molecule is always closely surrounded by other molecules. In general these surrounding molecules belong to the solid or liquid solvent in which the active material is dissolved. If we have to deal with the luminescence of a pure substance (if such cases occur), the surrounding molecules are of the same kind as those which participate in the luminescence phenomena. But in either case the period of vibration will be different from what it would be if the vibrating molecules were isolated. Since the change in period will be relatively great for those molecules that are close to their neighbors and smaller for those that are further away, it is seen that the natural period will vary through a considerable range as the active molecules move about, and at each instant there will exist in the substance molecules having all periods lying between certain rather wide limits. The absorption spectrum of the substance therefore consists of bands rather than of lines.[1]

When a molecule is dissociated by the action of the exciting light, the two parts, being electrically charged, will be more strongly attracted by the molecules of the solvent than was the original neutral molecule. Recombination of the separated ions is therefore more likely to occur when the latter are in the immediate neighborhood of the molecules of the solvent, *i. e.*, under conditions which make the period of the resulting vibrations longer, on the whole, than the period natural to the active molecules before dissociation. Since recombination can occur under a variety of conditions a wide range of wave-lengths will be represented in the luminescence spectrum; the latter also will consist of bands rather than of lines.

[1] Essentially this explanation of the broadening of spectral lines has been discussed in some detail by Galitzin, Wied. Ann. 56, p. 78, 1895.

But on the whole the wave-length of the light emitted during luminescence will be longer than that of the exciting light. The same sort of thing will occur, although in less marked degree, even when the active molecule is itself electrically charged, as in the case of fluorescein. In this case, as well as in that first considered, it may even be that each of the two parts into which the active molecule is dissociated becomes a nucleus to which neutral molecules are attracted so that the ions become heavy aggregations of molecules. This is the assumption usually made regarding the production of ions in gases by the action of Roentgen rays, cathode rays, etc. If this is the real condition of affairs, the reasons for increased wave-length in the light emitted are still more evident.

It will be seen that this way of looking at the phenomena of photo-luminescence gives what might be called a mechanical explanation of Stokes' law. It does not lead us to expect, however, that Stokes' law will always be *exactly* followed. The luminescence spectrum and the absorption spectrum may overlap; in fact, it is to be anticipated that they will do so in the majority of cases. This is in agreement with the more recent experiments on this subject.[1]

Among the other experimental laws of photo-luminescence that are satisfactorily accounted for by the theory of Wiedemann and Schmidt may be mentioned the fact that the form of the luminescence spectrum is the same whatever may be the wave-length of the exciting light.[1] Light corresponding to any part of the absorption band may, if sufficiently intense, produce dissociation. But the manner in which recombination occurs will not depend in any way upon the wave-length of the rays by which the dissociation was produced.

Upon the basis of this theory it is clear also that we should expect no change in the form of the phosphorescence spectrum during decadence. The intensity of phosphorescence will depend at each instant upon the number of recombinations that occur per second, and will therefore diminish as the number of free ions becomes less. But it seems probable that the number of recombinations that occur under such conditions as to give light of a certain wave-length will still remain the same fraction of the whole

[1] Nichols and Merritt, PHYSICAL REVIEW, Vol. 18, p. 403, 1904.

number. The case has some resemblance to that of the distribution of velocities among the molecules of a gas; if the total number of molecules in a given volume is diminished, the number having a given velocity will also diminish; but this number will still be the same fraction of the whole.

The simplest hypothesis regarding the law of recombination of the ions in a luminescent substance is that which has been applied to the case of ionization in gases.[1] Let the number of positive ions present per c.c. at any time t be n. The number of collisions between a positive and a negative ion will be proportional both to the number of positive ions and to the number of negative ions; and a certain fraction of these collisions will result in recombination. Since positive and negative ions are present in equal numbers we have

$$\frac{dn}{dt} = -\alpha n^2,$$

$$\frac{1}{n} = c + \alpha t \quad \text{where} \quad c = \frac{1}{n_0}.$$

Since the intensity of phosphorescence is proportional to the number of recombinations per second

$$I = k\alpha n^2 = \frac{k\alpha}{(c + \alpha t)^2}.$$

This is one form of the expression originally proposed by E. Becquerel to express the decay of long time phosphorescence, and is the same law that was derived on the basis of entirely different theoretical assumptions by H. Becquerel.[2] As was shown in the first part of this paper the equation represents satisfactorily the results of our own experiments with Sidot blende.

In comparing our experimental results with the law just derived it was convenient to write the above expression in a different form: namely

$$\frac{1}{\sqrt{I}} = a + bt$$

where

$$a = \frac{1}{n_0\sqrt{k\alpha}}; \quad b = \sqrt{\frac{\alpha}{k}}.$$

[1] Rutherford, Philosophical Magazine, Vol. 44, p. 422, 1897.

[2] Comptes Rendus, Vol. 113, p. 618, 1891.

It is to be remembered that if I refers to the intensity at some particular part of the phosphorescence spectrum, k must be regarded as a function of the wave-length.

The fact that the experiments indicate a linear relation between the time and $I^{-\frac{1}{2}}$ has already been pointed out, and reference to the tables on pages 284–5 shows that the differences between the computed and observed values of t, which are usually small, are entirely unsystematic. It is possible to test the law still further by considering the values of the constants a and b. Except in the case of the last curve of Table I., the data refer to curves of decay for different wave-lengths, but with the same excitation. a and n_0 are therefore constant, while k depends upon the wave-lengths. It will be noticed that

$$\frac{a}{b} = \frac{1}{n_0\sqrt{ka}} \cdot \sqrt{\frac{k}{a}} = \frac{1}{n_0 a}.$$

This quotient should therefore be a constant for all curves taken with the same excitation and under similar experimental conditions. The values of the ratio a/b for the three curves of Table III. show considerable variation from equality, being 1.5, 2.0, and 1.7. The values of the ratio for the first three curves of Table I. are 1.73, 1.75 and 1.65. In view of the difficulty of maintaining constant conditions in the experiments on phosphoresence the agreement between these three values is highly satisfactory. As already stated the observations at 0.483 μ in Table II., probably on account of some experimental error, cannot be represented by the expression here considered, so that the value of a/b for this curve cannot be determined. But for the curves taken at 0.512 μ and 0.547 μ (Table II.) the quotient a/b has the values 2.32 and 2.43, respectively. Here, too, the agreement is all that could be expected.[1] Our results therefore afford strong confirmation not only of the conclusion reached in our last communication that all parts of the green band decay at the same rate, but also of the general theory of phosphorescence that we have used in deriving the law of decay.

The data permit still another test of the general theory, the result

[1] There is no reason why the values a/b for Table I. should be the same as those for Table II. or III. since the observations were made several weeks apart, and with no attempt to keep the intensity of the comparison source the same in the different cases.

of which is less satisfactory. It will be remembered that in the case of the fourth curve of Table I. the exciting light was less intense than that used with the other curve for 0.512 μ. The observations for the fourth curve were made on the same day as those for the second curve, and although the former were made in the afternoon and the latter in the forenoon, every attempt was made to keep the comparison source the same in the two cases and to have all the other experimental conditions as nearly as possible constant. If we compare the two curves for 0.512 μ in Table I., we see that a and k have the same value for both, while n_0 is different. The constant b, however, is independent of n_0. This constant should therefore have the same value for both curves; in other words the straight lines obtained by plotting $I^{-\frac{1}{2}}$ should be parallel. As a matter of fact the values of b determined for the two curves are 0.045, for the second curve of Table I., and 0.052 for the fourth. The fact that the two values are unequal is shown in Fig. 37 by the lack of parallelism of the two lines A' and B'.

The law of decay derived upon the basis of the simple considerations outlined above, while representing the results of observation during the early stages of phosphorescence with surprising accuracy, can not be regarded as more than a first approximation to the correct expression. When the curve of decay is followed for several minutes instead of for several seconds a systematic variation is found from the linear relation between $I^{-\frac{1}{2}}$ and t. Experiments dealing with the long-time phosphorescence of Sidot blende and certain other substances will be described in our next paper.

A METHOD OF CALIBRATING GAS METERS.[1]

BY FRANCIS GANO BENEDICT.

FOR physical or physiological experimenting, gas meters in which the revolving metal drum is partially immersed in water are frequently used. One of the best forms is that made by S. Elster,[2] of Berlin. The drum of this meter is connected by gear wheels to dials which register the quantity of gas passing through it. This type of gas meter is much more accurate than are the so-called "dry" meters, but its readings require numerous corrections, such as those for temperature, barometric pressure, tension of aqueous vapor, tension of the gas in the meter, rate of flow and finally, for possible mechanical inaccuracies in the registering device of the meter itself.

Inasmuch as all meters are subject to variations in mechanical accuracy and especially to the variations due to the rate of flow, it is necessary to calibrate each meter and compare the readings obtained from the dials with the true volume of gas passed through the meter. In order to calibrate accurately, therefore, a mechanical gas meter, it is necessary to know with great exactness the true volume of gas which is passed through it.

The usual method of ascertaining the true volume of gas is by means of some form of aspirator, from which the air can be forced through the meter or into which it can be drawn. The use of an aspirator is, however, unfortunately subject to considerable error. In the first place, there may be marked changes in the temperature of the aspirator itself, especially if it be of any considerable size. As a matter of fact, this possible error has restricted the size of aspirators to such an extent that it is rare that an aspirator containing over ten liters can be used advantageously. Consequently, the

[1] Contribution from the Chemical Laboratory of Wesleyan University.

[2] For a description and diagrams of the construction of the Elster type of meter see v. Flügge, Hygienische Untersuchungsmethoden, Leipzig, p. 351, 1881.

total volume of air passed through the meter and used for checking its accuracy may not exceed ten liters whereas the meter itself may be designed to record several thousand liters. Furthermore, in spite of the fact that the Elster meter is so devised as to require a minimum pressure to rotate the drum and dial, it is a fact that at the beginning of each calibration there is a period when there is a gradually increasing pressure of the gas inside the system, and at the end, a similar falling off in pressure. These two inequalities in large measure compensate, but on so small a volume as ten liters they may result in an appreciable error.

In this laboratory, an Elster meter is made use of in determining the carbon dioxide and water content of the residual air inside a large respiration chamber containing about 5,000 liters. For this purpose a sample must be drawn in not more than three or four minutes which should not exceed ten liters. As a result the analyses made on this sample must be multiplied by a very large factor, *i. e.*, 500, in order to give the true amount of carbon dioxide and water vapor inside the respiration chamber, and this necessitates great care in the calibration of the meter. While undoubtedly an aspirator method when accurate in all its details [1] would give a calibration which would be perfectly satisfactory for our purpose, another method for ascertaining the true volume of gas passed through the meter has been used in this laboratory.

In principle the method is as follows: Oxygen from a weighed cylinder of the highly compressed gas is allowed to pass through the meter. The volume of the issuing gas is computed from the loss in weight in the cylinder and the known weight of a liter of oxygen, making due allowance for the barometric and thermometric conditions of the experiment.

It is possible to obtain in the market, small steel cylinders filled with highly compressed oxygen.[2] The oxygen is not absolutely pure, containing besides three to seven per cent. of nitrogen, small

[1] A special form of aspirator (ten liters), provided with protection against sudden temperature fluctuations, has been devised by N. Zuntz. (See Untersuchungen über den Gaswechsel und Energieumsatz des Radfahrers. Leo Zuntz, Berlin, p. 8, 1899.

[2] Several hundred of these cylinders have been used in this laboratory during the past three years. They are obtained from the S. S. White Dental Mfg. Co. at Prince's Bay, Staten Island, N. Y.

amounts of water vapor and carbon dioxide, but if the gas leaving the cylinder is conducted first, through soda lime, and second, through sulphuric acid, the gas leaving the exit tube of the apparatus will consist of pure oxygen and nitrogen, the proportions of which can be readily found by the usual gasometric analyses.

The cylinders contain ten cubic feet (283 liters) of gas and weigh when filled with gas about fifteen pounds (seven kilograms). A balance at once large enough to support a load of ten kilograms and sensitive enough to detect small differences in weight is made in Germany by Sauter.[1] The balance can be considerably overloaded, so that it is capable of weighing the oxygen cylinder and purifying attachments with a total weight of somewhat more than ten kilograms to within ten to twenty milligrams. Since the weight of one c.c. of oxygen is 1.43 mgms., the total volume of gas leaving the cylinder can be computed from the weight to within 7 to 14 c.c. In one of these steel cylinders there are compressed 283 liters and it is thus seen that it is possible by this means to measure the volume of 283 liters of gas to within 30 c.c., an accuracy that cannot be obtained by any other means of securing so large a known volume of gas with which the writer is familiar.

The details of manipulation are as follows:

An oxygen cylinder to which the regular connection is attached is supplied with two U-tubes, one containing soda lime and the other sulphuric acid, connected in series and with the oxygen cylinder. On opening the valve the oxygen flows through the two tubes and is thereby deprived of its carbon dioxide and water. Inasmuch as the valves on the oxygen cylinder are not so constructed as to control the enormously high pressure of 1,800 pounds with the greatest fineness, it is best to introduce some device for preventing the loss of gas in a sudden rush through the U-tubes. This result has been found to be obtained by placing a rubber bag, *i. e.*, a common foot-ball bladder, in a T-tube between the yoke connection and the first U-tube. The oxygen cylinder with its fittings is then weighed,

[1] Three such balances, obtained through the Bausch and Lomb Optical Co., are in use in this laboratory, the smallest one weighing to ten kilograms with a sensitiveness of less than ten milligrams. This balance in a glass case cost delivered in Middletown, Conn., duty free, but about sixty dollars.

using a counterpoise and ordinary brass weights. The purifying devices are attached directly to the cylinder by means of stout rubber bands and are weighed with the cylinder.

A rubber tube leads from the sulphuric acid U-tube and conducts the dry, carbon-dioxide free gas into the meter which is to be calibrated. From 10 to 283 liters of gas may be passed through the meter and the readings on the dial carefully recorded. By means of the valve on the oxygen cylinder and the rubber bag, it is possible to maintain a very constant flow of gas at any desired rate. It has been repeatedly proved that with the Elster meter, the gas passing through at the rate of three liters per minute is completely saturated with water vapor and consequently the tension of this water vapor may be correctly determined by knowing the exact temperature of the gas. Experiment has shown that the temperature of the gas in the meter is that of the water in the meter. A thermometer graduated in tenths of a degree and read to hundredths is inserted in the meter and gives this temperature. The barometric pressure is read at the beginning and the end of the experiment and the tension of the gas in the meter is noted by a water manometer attached to it. From the data regarding barometric pressure, temperature of the meter, tension of the gas in the meter and loss in weight of the oxygen cylinder, the true volume of gas passing through the meter may be computed and compared with the reading on the dial.

In the computation of the true volume of gas issuing from the cylinder the following data are used :

Weight of one liter of oxygen under standard conditions of temperature and pressure and at the latitude of 45° = 1.42900.[1] This corrected for the value of g at Middletown (41° 34″) becomes 1.42853 grams.

In calculating the weight of one liter of atmospheric nitrogen at Middletown the ratios between the weights of oxygen and nitrogen as found by the three observers, Von Jolly, Leduc and Rayleigh,[2]

[1] Morley, Smithsonian Contributions to Knowledge, **980**, p. 111, 1895.

[2] The values found by these three observers are given by Rayleigh and Ramsay in their monograph, "Argon. A new constituent of the atmosphere," Smithsonian Contributions to Knowledge, **1033**, p. 14, 1896.

are compared with the weight of one liter of oxygen at Middletown in the following manner :

$$\text{Von Jolly,} \quad 1.42853 \times \frac{1.25819}{1.42971} = 1.25715 \text{ grams}$$

$$\text{Leduc,} \quad 1.42853 \times \frac{1.25709}{1.42910} = 1.25659 \text{ grams}$$

$$\text{Rayleigh,} \quad 1.42853 \times \frac{1.25718}{1.42952} = 1.25631 \text{ grams}$$

$$\text{Average of 3} = 1.25668 \text{ grams}$$

It is thus seen that one liter of atmospheric nitrogen under standard conditions of temperature and pressure and corrected for gravity at Middletown weighs 1.25668 grams.

The loss in weight of the oxygen cylinder gives the weight, not of pure oxygen, but of the weight of oxygen containing a known percentage by volume of nitrogen. It is possible to compute the weight of one liter of gas of the composition represented by that in the cylinder by means of the above factors and by means of the percentage composition of the oxygen as determined by the gasometric analyses.

An example of this calculation is here given : Cylinder No. 38367 contained 96.144 per cent. oxygen and 3.856 per cent. N by volume.

96.144 liters of oxygen $\times$ 1.42853 = 137.34 grams.
3.856 " " nitrogen $\times$ 1.25668 = 4.85 grams.
100 " " mixture weighs 142.19 grams.
Or 1 liter weighs 1.4219 grams.

Consequently the loss in weight of the cylinder divided by the weight of one liter of the mixed gases gives the volume of the gas that has been removed from the cylinder.

The meter was calibrated under conditions similar to those in which it is ordinarily used. Air was forced through the meter at a rate of about 3 liters per minute. After leaving the meter it was caused to bubble through concentrated sulphuric acid. Thus there was normally a pressure on the air in the meter corresponding to the pressure required to force 3 liters of air per minute through the layer of sulphuric acid in the drying bottle. This pressure was measured by a water manometer and was not far from 80 mm. of water.

A sample calibration follows:

Reading of meter at end	= 93.374 liters
" " " " start	= 2.492 liters
	90.882 liters.
Temperature of Meter 20.13.°	Manometer = 80 mm. water = 5.88 mm. Hg.
Barometer at begin. (4.54 P. M.)	= 754.30 mm.
" " end (5.27 P. M.)	= 754.20 mm.
Average	= 754.25 mm.
Manometer correction	= 5.88 mm.
Sum	= 760.13 mm.
Tension water vapor at 20.13°	= 17.50 mm.
	742.63 mm. corrected pressure.

$$90.882 \times \frac{1}{1 + \alpha 20.13} \times \frac{742.63}{760} = 82.695 \text{ liters.}$$

The weight of the oxygen cylinder at the beginning of the calibration was equal to that of

The counterpoise	+ 2,712.25 grams.
At end "	+ 2,594.25 grams.
Weight of Oxygen + Nitrogen	= 117.30 grams.
117.30 ÷ 1.4219	= 82.496 liters.

Consequently the meter reading is slightly higher than the true value, the correction factor being obtained from the ratio between 82.695 and 82.496. All meter readings obtained at the rate of flow and pressure conditions observed here, therefore, are to be multiplied by the factor 0.9976.

In conclusion I wish to acknowledge my indebtedness to Miss Charlotte R. Manning, of this laboratory, for her assistance in conducting the tests of this method.

MIDDLETOWN, CONN.

ON THE GEYSER IN ATAMI, JAPAN.

BY K. HONDA AND T. TERADA.

THE remarkable phenomena of the periodic eruptions of geysers have attracted the attention of many observers. Mackenzie [1] observed the Great Geyser of Iceland in 1811 and tried to explain the phenomenon. But his theory proved unsatisfactory. Bunsen [2] visited the same geyser in 1847 and proposed his well-known theory of the vertical pipe. Müller [3] constructed a model after Bunsen and showed that it worked periodically if two portions of the vertical pipe be heated. This theory, however, is not free from objections. Contrary to Bunsen's view, O. Lang [4] considered the seat of eruption to lie at a great depth below the vertical pipe, the water in which acted as a valve for the enclosed vapor. Models given by J. Ziegler [5] and G. Wiedemann [6] explain the phenomenon of the geyser from a similar point of view. Other models by J. Petersen, A. Andreae and others [7] do not differ much in principle from those just referred to. The experimental investigations of Andreae [8] and H. Ebert [9] show

[1] Mackenzie, Travels in Iceland, 1811.

[2] Bunsen, Physikalische Beobachtungen über die hauptsächlichsten Geysir Island, Gehlers Physikalisches Wörterbuch (2 Auflage), LXXII.; Pogg. Ann., 72, 1847.

[3] Müller, Lehrbuch der Kosmischen Physik, Braunschweig, 1894, S. 619.

[4] O. Lang, "Ueber die Bedingungen der Geysir," Göttinger Gelehrten Nachrichten, 1880, S. 225.

[5] J. Ziegler, Vorträge des phys. Vereins in Frankfurt a. M., 1872, demonstrated by Dr. Nippoldt.

[6] G. Wiedemann, "Ueber einen Apparat zur Darstellung der Erscheinungen der Geysir," Ann. der Physik und Chemie (2), XII.

[7] J. Petersen, "Darstellung der Geysir Erscheinungen," Neues Jahrbuch für Mineralogie, Geologie and Palāontologie, 1879, II.

A. Andreae, "Ueber einen künstliche Nachbildung der Geysirphānomene," Ibid., 1893, II.

K. Antolik, Zeitschrift f. d. Phys. u. Chem. Unterr., 1890–91.

A model given by A. C. Munby, Nature, 65, p. 247, is of a somewhat different principle.

[8] Andreae, loc. cit.

[9] H. Ebert, "Versuch mit dem G. Wiedemannschen Geysirapparate," Annalen d. Phys. u. Chem. (2), LXIII.

that by properly modifying different parts of the models, several types of natural geysers can be imitated. The latter, however, remarks that such a simple theory is not able to explain all the diversities in the manner of eruption observed in numerous geysers in Iceland, North America and New Zealand.

Different from other geysers, the geyser of Atami in the province of Izu is characterised by the regularity of the eruption, which consists in alternate projections of hot water and steam, usually five times in succession. The water projected does not return to the orifice as it does in several other geysers. The orifice, which originally opened vertically upward, has been covered by a heap of stones to prevent the dangers caused by the eruption. At present three orifices are exposed, among which one is distinguished as the principal opening. Besides, there is another mouth hidden underground ; the water projected by these orifices is distributed to several bath-houses by conduits. The water is of a strong saline taste, containing about ½ per cent. of sodium chloride, *i. e.*, about one fifth of that contained in the sea water. The mouth of the geyser is not far from the sea coast and about 22 m. above the sea-level.

The eruption occurs usually five times in a day and night. During the time of repose, we see only a small quantity of steam rising from the mouth. As the time of the eruption approaches, a rumbling sound is heard underneath. The boiling water appears just inside the mouth. It soon retires and again appears. This state continues for about three quarters of an hour. Next a small quantity of hot water flows out intermittently. This is followed by an intermittent stream of moderate quantity with a longer period. The activity soon attains its maximum. A torrent of hot water gradually increasing in force is torn into a violent splash and projected with a great velocity by steam which gradually increases with the diminishing water. When the roaring sound of steam reaches the maximum, the water almost disappears. The steam now diminishes and is soon followed by the second gush of water. After these states have been repeated five or six times, the activity ends with the last steam which gradually subsides into an inconsiderable amount as seen at the beginning. It takes above two hours from the beginning to the last stage of the eruption. The time of repose

is a little less than three hours on the average. These regular recurrences are often interrupted by an abnormal outburst, called *nagawaki*, at which the water and steam come out incessantly for above twelve hours and after which a long repose follows as a rule. In years rich in this anomaly it occurred almost monthly, whereas in the last few years only once or twice.

Our excursion to Atami was undertaken to make detailed observations as to the manner of eruption and if possible to get an insight into the internal mechanism of the geyser. Arrangements were contrived to keep records of the manner of each successive eruption.

A pendulum consisting of a brass rod and a heavy lead ball was hung before the principal orifice. The water and steam, projected nearly horizontally, deviate the pendulum by the impulsive pressure. The motion of the pendulum was transmitted by a cord and pulley to a recording pen guided by two vertical pillars with grooves, in which roll two friction-wheels attached to the penholder. The vertical displacement of the pen was recorded on a cylinder making one revolution every two hours. The pendulum was afterward removed to a position where the impulsive action of vapor and splash was shielded off and the flow of water only could be recorded.

To record the manner in which the steam is ejected, an arrangement was used which was nothing more than an air-thermograph. A small cylinder of sheet zinc was introduced into a mouth neighboring to the principal orifice, where it was possible to find a position such that the bulb was exposed to the heating of the steam only. This orifice, being a smaller branch of the main one, could be considered as representing the main one on a reduced scale. The bulb was connected by a fine copper capillary tube to one of the arms of a U-tube containing mercury. The motion of the mercury meniscus in another arm was recorded on a cylinder by a pen mounted on a float on the mercury and guided by two vertical pillars with grooves and two friction-wheels attached to the penholder. To determine the temperature of the water and steam a maximum thermometer was used.

To take continuous records of the exact time of eruption, and also the general manner of each eruption, a mercury tide-gauge,

constructed after Mr. Nakamura's design,[1] was used. The lead pipe of the instrument was inserted to the neck of the geyser. The pressure of the projected water at the neck during each eruption was recorded on a cylinder revolving once every 24 hours. The automatic records of daily eruptions have been taken during the last two years.

In the following lines, a brief account of our results of observation is given.

I. Ordinary Eruption.

An ordinary eruption consists of three distinct series, termed conventionally the first, the second and the third, differing in period and force and succeeding one another very regularly. Fig. 1 is a reproduction of one of the records obtained by our pendu-

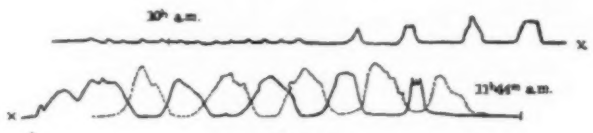

Fig. 1.

lum recorder. The abscissa represents the time, and the ordinate the deflection of the pendulum by the pressure of water. The dotted line shows the velocity of the steam obtained by our air-thermograph. The first series, which begins the outburst, consists of a small quantity of water appearing with an average period of 1 minute and 40

Fig. 2.

seconds. After this intermittence has been repeated a score of times the second series follows. A moderate quantity of water comes out three or four times with a mean period of six minutes. The water increases in quantity and force till at last the third or

[1] S. Nakamura, Proceedings of the Tokyo Physico-Mathematical Society, Vol. I., No. 15, p. 123, 1902.

principal series sets in. On the first outburst of the third series we see very often the superposition of the last one of the second series. The third series is to be distinguished from the previous series by its violence and the quantity of water and steam. The sequence of the water and steam occurs usually five or six times with a mean period of about 11 minutes. Fig. 2 is a record obtained by the mercury tide-gauge, and shows regular periodic sequence of eruptions with a mean period of 24/5 hours.

II. ABNORMAL ERUPTION; NAGAWAKI.

The first *nagawaki* recorded by our arrangement began at 4:30 A. M. on January 14, 1905, from the fourth eruption of the third series. During two or three days before the *nagawaki*, the period of successive eruptions seems to have been slightly diminished; but in such a degree that may be found not seldom in our records without leading to either *nagawaki*, or anything extraordinary. The *nagawaki* began, as it were, almost suddenly in the midst of an ordinary eruption. The flow of hot water continued without interruption, gradually decreasing in quantity and mixed with steam. At 7:40 P. M., it came to a sudden repose; at 2:40 A. M. on the 15th, an intermittent flow of hot water resembling the second series of an ordinary eruption began and continued for about three hours. After a repose of four hours ordinary eruptions at last set in, but with the period remarkably shortened and the activity strikingly reduced. The number of eruptions per day was ten, a remarkable contrast to the ordinary frequency of five. The frequency decreased afterward very slowly with the time, and recovered its original value after the lapse of about a month.

The second *nagawaki*, which occurred on May 26, was quite similar to the previous one in its general aspects, though it took place in conjunction with the extraordinary decrease of the general activity.

It is an interesting coincidence that the two *nagawakis* of January and May began at the same phase of the ordinary eruption at nearly the same hour of day, and that a center of low atmospheric pressure was approaching from the Pacific in each case.

III. Influence of Atmospheric Pressure.

Examining our records of long observation, we found a remarkable fact that low atmospheric pressure *retards* and high atmospheric pressure *accelerates* the eruption of the geyser. This curious fact may be seen from Fig. 3. Times of the successive eruptions are plotted as the ordinates corresponding to each day which is laid off as abscissa; corresponding points for successive days are connected into five broken curves (*b*)–(*f*). Curve (*a*) represents the daily change of the mean atmospheric pressure. The probable cause of the strange coincidence would be given later.

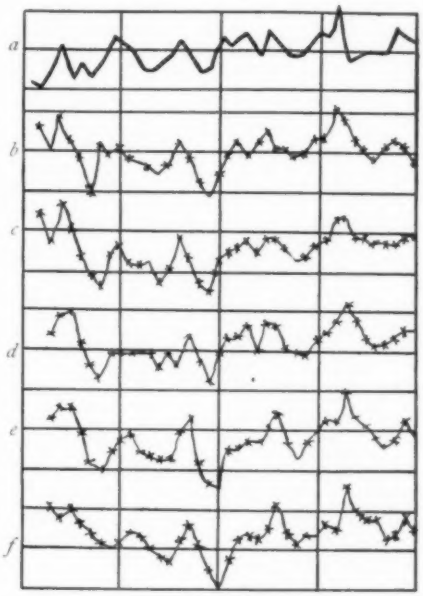

Fig. 3.

IV. Temperature of Hot Water During Eruption.

A maximum thermometer was placed about 1.5 m. inside theorifice and the temperature has been read daily since last April. It was found that the temperature at this depth was almost invariably 103°–104° C. At the orifice, however, it was about 100° C., indicating a rapid cooling of the hot water. Hence it may easily be conjectured how hot the underground water would be at a depth of some ten meters.

V. Velocities of Water and Steam.

The pressures of water and steam upon the bob of a special pendulum arrangement were recorded on the cylinder, and estimated afterward by the substitution of known weights. The total pressure upon a sphere is known to be approximately equal to one half of that upon a circular disk of the same diameter. Hence

$$p = \frac{\pi r^2 \rho v^2}{2}, \quad \text{or} \quad v^2 = \frac{2p}{\pi r^2 \rho},$$

where p is the pressure, r the radius of the bob, ρ the density and v the velocity of water or steam. For the water we obtained, at the mouth,

$$v = 1.5\text{–}2.0 \text{ m. per second,}$$

and for the steam

$$v = 18\text{–}24 \text{ m. per second,}$$

the velocities varying within the limits according to the phase of each eruption. In this calculation, we took for the value of ρ the density of saturated vapor under ordinary atmospheric pressure.

VI. Quantities of Water and Steam.

For the rough estimation of the quantity of water thrown out in an eruption, we measured directly the amount supplied to a number of tanks and calculated the total from the sections of several conduits. The quantity thus estimated amounts to 45 cubic meters.

The rough estimation of the quantity of steam was carried out in the following way:

Let the quantity of steam be denoted by Q. Then

$$Q = \int Sv\rho dt,$$

when S is the area of the orifice. If V be the ordinate in the curve representing the relation of velocity of steam to time, obtained by our special thermograph above referred to, we may put

$$v = kV, \quad \therefore \quad Q = S\rho k \int Vdt.$$

Since v was determined by the pendulum experiment, and the corresponding V from the thermograph curve, k can easily be known; by calculation, it was found to be 500. S was estimated to be 200 cm.^{2}; for an instance, we obtained

$$\int Vdt = 6{,}500, \quad \therefore \quad Q \doteqdot 500 \; kg,$$

the number must be considered as giving only the order of magnitude.

VII. Extraordinary Decrease of Activity.

During the course of the last few years, several wells have been bored in this district. Most of them give a moderate quantity of

hot water only by pumping. Since the last year, the number of wells was greatly increased, amounting to about twenty in all. Sawaguchi's well, bored on March 27 of this year, burst out with great violence, throwing up a column of hot water about 8 m. high. On May 22, another one, Yonekura's well, of greater activity, has been opened within a few hundred meters of the geyser, giving hot water at a rate of 310 cubic meters per day. Two days afterwards another one, Hignchi's well, of not much less activity, was bored. After the boring of the Sawaguchi's, a slight decrease in the frequency of the geyser was observed; on May 20 it was reduced to 4.4, though the force of each eruption presented no appreciable change. After the boring of the other two the frequency remarkably decreased; it was 3.6 on May 26. Moreover, the first and second series of each eruption became considerably longer and the principal series was considerably lessened in force. After the *nagawaki* of May 27, the frequency was temporarily increased; but on June 11, it fell again to 3.2. As shown in Fig. 4, the first and second series lasted for three and a half hours and

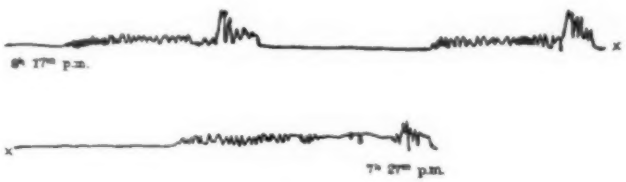

Fig. 4.

the third was reduced to only three weak eruptions. Consequent decrease in the quantity of hot water caused trouble to several bath-houses supplied by the geyser, and therefore the above three wells were all stopped — Yonekura's on June 12, Sawaguchi's on the next day and Higuchi's on July 12. The frequency of eruption has gradually increased since then, and in the middle of August, it attained 4.5 which is yet somewhat short of the original value. As for the mode of each eruption, it has quite recovered in force.

VIII. Level Change and Temperature of Wells.

Level change of two wells near the geyser were recorded by means of Honda's limnimeter. Nomura's well, which is within 200

m. of the geyser and quite high above the sea level, shows a regular up and down motion corresponding to the eruption and repose of the neighboring geyser. Effects of the tidal and atmospheric pressure are also recognizable, but not very remarkably. (Fig. 5.) The

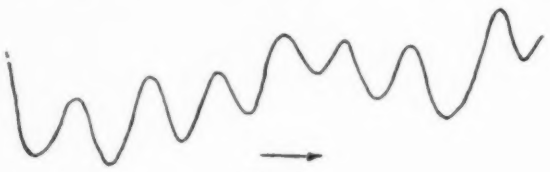

Fig. 5.

temperature of the water of this well is 50°–60° C. In Suzuki's well, which is more remote from the geyser than Nomura's, the effect of the geyser is not observed, but the level rises and falls with the tide. (Fig. 6.) The head of the water is 22 m. above the sea

Fig. 6.

level. Temperature measurement with a maximum thermometer was made in Abo's well, which is situated in the midway between the geyser and Yonekura's well. The results are tabulated as follows:

At the surface of water,	62°.0 C.
23 m. below,	95°.5
28.5 m. "	98°.3
29.7 m. "	104°.7
31.0 m. "	118°.2

Thus, a remarkably high temperature was found to exist in the surface layer of the district.

IX. Explanation of the Phenomena.

Existing theories on geysers fail to explain the exact manner of eruption of the geyser of Atami. After a series of experiments with several forms of models, we arrived at a theory which we hope may fairly explain the phenomena of the geyser in question.

Referring to Fig. 7, A is a cavity lying in a considerable depth; a is the vertical pipe and b a canal which supplies the water to A. We conceive a side canal c intermediate between A and a, which leads to a second cavity C, not shown in the figure. The temperature of the water in a and c is supposed to be lower than the corresponding boiling point. Water in A is heated by the wall of the cavity, the temperature of which is supposed to be decidedly higher than the boiling point at the depth. The source of the heat is probably to be attributed to the hot water and steam running through numerous veins and canals extending in the depth of the district. When the tension of the vapor in the cavity attains a critical value, the water is thrown off and then the steam follows. When a certain amount of steam is given off, the pressure in the neck is reduced to such a degree that the water flows in from the side canal and stops the eruption momentarily. Soon the downward pressure of the water column is overcome by the tension of vapor and the second gush follows. These eruptions are repeated several times, till the vapor pressure is so reduced as to admit the comparatively colder water from the feed canal b and also from c. Thus the activity is quenched for a while till the next eruption begins. A model (Fig. 8) constructed according to this view, worked very satisfactorily. The manner of eruption was imitated in many details.

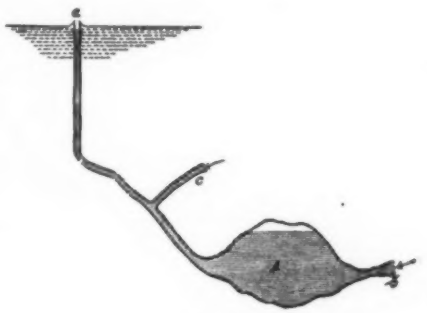

Fig. 7.

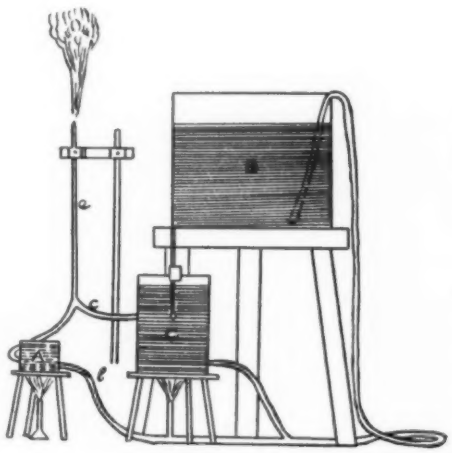

Fig. 8.

The number of intermittences in an eruption increases with the temperature of the water in *c*.

The phenomena of *nagawaki* may be explained partly by the supposition that the underground temperature is raised above its normal value and so the temperature of the cavity *C* becomes higher than the ordinary case. If the temperature of the cavity *C* in our model be raised to a certain value, the eruption corresponding to *nagawaki* begins. It resembles the actual one even in some details. The cause of this occasional change of temperature is probably the change of the subterranean volcanic activity which keeps the underground temperature in this district considerably above the boiling point of water.

The fact that the frequency of eruptions immediately after *nagawaki*, is nearly doubled, may partly be explained, if we consider that the temperature of the heating cavity was raised during the course of the *nagawaki* by the incessant flowing of superheated water from a great depth. It may be added as a very suggestive fact that if in our model, a quantity of air be blown into the heating cavity, the frequency of eruption increases at first remarkably and gradually decreases with the gradual expulsion of air by successive eruptions; even the weakness of activity in the actual case is imitated with great faithfulness. During a few hours after *nagawaki*, the cavities as well as the canals leading to the orifice remain drained out, so that it is possible that air or other gases may enter into the cavities and cause the increased frequency of the eruption.

It is a common fact of observation that the temperature of some ordinary hot springs rises with low atmospheric pressure. This is undoubtedly due to the increase of flow due to the enhanced circulation of water caused by the reduction of the pressure. If in the supposed heating cavity of the geyser, the interchange of water due to the slow circulation through numerous veins and fissures (not shown in the figure), be accelerated by some cause, the time required for the sufficient heating for eruption must necessarily be prolonged. This consideration seems to explain partly the influence of atmospheric pressure on the period of eruption above mentioned. Again, the possible influence of well-boring on the geyser, may be explained on the same basis. Such a well may increase the circu-

lation of underground water in its vicinity and result in the retardation of the eruption of the geyser in a similar manner. Moreover, it is quite natural that the hot water should find its easier vent through a new passage opened with a less resistance, at the expense of the quantity originally given out by the old one alone. The prolongation of the first and second series of an eruption, suggests the slowness with which the pressure in the heating cavity approaches the critical value. The careful investigation of the variation of the frequency in connection with the boring and stopping of the wells, leads us to the strong belief that the striking coincidence of the well-boring and the decrease of the activity of the geyser, is a necessary, and not an accidental one. If the frequency of eruption does not yet quite attain its former value long after the stopping of the wells, we need not wonder at all, since some irreversible change in the subterranean mechanism might have happened during the period of the anomaly.

PHYSICAL LABORATORY,
IMPERIAL UNIVERSITY, TÔKYÔ,
December 28, 1905.

ON AN EMISSION OF NEGATIVELY CHARGED PARTICLES PRODUCED BY CANAL RAYS.[1]

BY L. W. AUSTIN.

THE work described in the following paper was undertaken for the purpose of studying the possible secondary radiations produced by the impact of the canal rays on a metal. Since it is known that the canal rays consist of positively charged particles of molecular dimensions travelling with a velocity sometimes exceeding 10^8 cm./sec.,[2] it seemed probable that they might give rise to reflected positive rays analogous to the reflected cathode rays studied by several physicists,[3] and perhaps also to an emission of negative particles.

The tube used in the work is shown in Fig. 1. It was divided into two parts A and B. The part A was 7 cm. long and 2.5 cm. in diameter. B was 7 cm. in diameter and was separated from A by the system of brass diaphragms d with openings 2 mm. in diameter. The aluminum electrode e formed the anode while the front of the diaphragms served as cathode. The canal rays passed backward through the openings in the diaphragms into the observation space B, which was lined with fine brass netting. This with the diaphragms was connected to earth, thus forming an enclosed space practically free from the direct influence of the discharge. In looking for the reflection of the canal rays the following arrangement was used. A small brass cylinder C, 1.5 cm. in diameter and 1 cm. long, closed except for an opening 4 mm. in

Fig. 1.

[1] Read before the Washington Philosophical Society, February 10, 1906.

[2] W. Wien, Wied. Ann., Vol. 65, p. 440, 1898; Ewers, Wied. Ann., Vol. 69, p. 167, 1899; Austin, Bulletin of Bureau of Standards, Vol. 1, p. 439, 1905.

[3] Goldstein, Wied. Ann., Vol. 15, p. 254, 1882; Campbell Swinton, Proc. Roy. Soc., Vol. 64, p. 377, 1899; Starke, Wied. Ann., Vol. 66, p. 49, 1898; Ann. d. Phys., Vol. 3, p. 75, 1900; Austin and Starke, Ann. d. Phys., Vol. 19, p. 271, 1902.

diameter in the front, was fastened to a brass spindle. To the other side of the spindle was attached a brass disk R, 1.5 cm. in diameter. The spindle passed up through a ground glass joint and was connected to earth through a D'Arsonval galvanometer giving one division for 2.3×10^{-9} amp. This was shunted so as to have a lower sensibility during most of the work. The spindle could be turned so that the canal rays could be made to enter the cylinder C or strike the reflector R. In case the rays entered the cylinder all of the positive charges conveyed by them were caught and conducted to earth through the galvanometer. When the reflecting disk R was turned toward the rays the reflected portion would rebound and only the charges carried by the absorbed portion would pass through the galvanometer to earth. The difference in the currents indicated by the galvanometer in the two cases would represent the reflected portion of the rays.

The current for the tube was supplied by a motor-driven electrical machine with four moving plates capable of generating about 0.0003 amp. when driven at full speed. The amount of current could be varied at will by changing the speed of the machine. The difference of potential between the electrodes of the tube was measured by means of a Braun electrometer having a range of 500 to 10,000 volts. The vacuum was produced by a motor-driven Geryk oil pump.

The first observations showed that the reflection of the canal rays was entirely masked by a secondary negative emission, for the reflector current was found to be larger than the cylinder current.

As the work progressed it became evident that there were irregularities in the phenomenon of a very puzzling character. It was found that from time to time the ratio of reflector current to cylinder current varied between rather wide limits, and that these variations did not depend as far as could be observed either on the amount of current flowing or on the degree of vacuum and difference in potential between the electrodes. These irregularities have made it impossible to carry out the work with the same quantitative exactness as in the case of the cathode rays.

Irregularities have also been observed by Wien[1] in his determi-

[1] W. Wien, loc. cit.

nation of the ratio e/m for the canal rays, and it seems possible that they may arise in both cases at least in part from common causes. As an explanation of Wien's results, J. J. Thomson has supposed that perhaps some of the positive particles have their charges neutralized by taking on negative electrons as they pass through the gas, and that they again become ionized when they strike against a solid and are thus able to produce fluorescence. If we suppose that such neutral particles are also capable of producing the negative emission we have a possible explanation of our irregularities, for the presence of these neutral particles could not in any way be discovered in the cylinder while they would produce a difference in the reflector current. Another difficulty in quantitative measurements with canal rays lies in their great absorption in thin layers of foreign substances on the surfaces struck by them.[1] Notwithstanding these difficulties observations made on the same day and without introducing air into the tube generally agreed within a few per cent.

If we call the galvanometer current from the cylinder C and from the reflector R, $(R - C)/C$ will represent the ratio between the emitted negative particles minus the reflected positive particles and the positive particles producing them. In Table I. are given the mean values of series taken on three different days. Observations were

TABLE I.

Discharge P. D. Volts.	Galvanometer Deflections. 10^{-7} amp.		$\frac{R-C'}{C}$
	C	R	
7,000	78	114	0.46
7 000	102	146	.43
6,000	77	109	.42

[1] In this connection the following experiment was carried out: Two brass reflectors were carefully polished and cleaned with alcohol and then fastened to the two sides of the spindle in the tube. When struck by the canal rays both gave almost identical galvanometer deflections. One of the reflectors was then removed and rubbed over with the thinnest possible film of pump grease. When the reflectors were again compared the greased one gave a galvanometer deflection of only 0.5 cm., while the bright one gave 18 cm. When the machine was reversed so that cathode rays struck the reflectors it was found that the grease film was almost without effect and that the two deflections were practically identical. Even after rubbing the greased reflector as clean as possible with a dry flannel cloth, it still gave only about half the full deflection for the canal rays.

also made on other reflectors than brass. Cu gave practically the same results, Pt a larger relative negative emission and zinc a smaller one. But as observations with external E.M.F. in the galvanometer circuit showed that the conductivity in the space exposed to the canal rays was very high, so that a difference of potential of one volt between the reflector and earth produced a deflection amounting to a large fraction of the total effect due to the caanl rays, it was not thought best to put too much weight on these observations in which different metals were immersed in the conducting gas. For in this case it seems possible that the two metals would develop differences of potential as when immersed in an electrolyte.[1]

Since it is known that the negative emission produced when cathode rays strike a metal increases rapidly as the angle of incidence increases,[2] observations were made to determine whether this was also true in the present case. As the spindle bearing the reflector could be rotated it was possible to cause the canal rays to strike at any desired angle.

Table II. shows a set of these observations. It is seen that the galvanometer current increases rapidly as the angle of incidence increases, being more than 40 per cent. greater at 70° than at 0°.

TABLE II.

Angle of Incidence.	Galvanometer Deflections. 10^{-7} amp.
0°	156
40	170
60	196
70	223

And if we assume that the increase is entirely in the emission the difference amounts to about one and one half times.

In order to still further establish the existence of the negative emission and observe it directly the following arrangement was adopted : A cyclinder was constructed with the base insulated from the remaining portion by a hard rubber ring as shown in Fig. 2. Either part could be connected to earth through the galvanometer while the other was earthed directly. Any negative particles sent

[1] S. Arrhenius, Wied Ann., Vol. 33, p. 638, 1888.

[2] Austin and Starke, loc. cit.

out from the base when struck by the canal rays were caught by the part a and could be detected by being led to earth through the galvanometer. When the experiment was performed it was found as was expected that while the base b gave a positive deflection as before, the part of the cylinder a showed a negative current. Table III. gives the mean value of three sets of observations taken on

TABLE III. (See Fig. 2.)

Discharge P. D. Volts.	Galvanometer Deflections. 10^{-7} amp.		$\frac{a}{b-a}$
	b	a	
4,000	+ 6.8	−1.9	0.38
"	7.5	2.2	.41
"	18.0	5.6	.42

different days. The ratio of negative emission minus reflected positive particles to canal rays is now expressed by $a/(b-a)$ and the agreement with the results of Table I. is good.

Besides the Volta effect already mentioned there were two other possible spurious causes of the phenomenon, namely the presence of cathode rays mixed with the canal rays due to oscillations in the circuit and the action of ultra-violet light coming through the diaphragms from the discharge portion of the tube. As a magnetic field in the observation space strong enough to divert any cathode rays from the reflector had no effect on the emission, and as all action in the observation space ceased when the cathode rays in the discharge tube were diverted so that the canal rays did not pass the diaphragms these possible sources of error were considered eliminated.

The velocity of the new emission seemed to be a question of considerable interest, and accordingly attempts were made to determine it approximately by the method of magnetic deflection. In the first experiment a brass plate p, 1.5 cm. long and 1 cm. wide, insulated from the spindle was placed 1 cm. above the center of the reflector R as shown in Fig. 3. R was connected directly to earth and p to earth through the galvanometer. A second experiment was arranged as in Fig. 4. Here the plate p was parallel to

the reflector and separated from it by an earthed brass screen *S*. The magnetic field was produced by a horseshoe magnet and of course was not at all uniform. The strength of the magnet may be estimated from the observation that when brought within 3.5 cm.

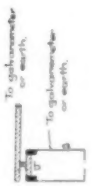

Fig. 2.

Fig. 3.

Fig. 4.

of the axis of the discharge portion of the tube the cathode rays at a potential of 4,000 volts were bent on a radius of about 4 cm. The results of the two experiments are shown in Tables IV. and V.

TABLE IV. (See Fig. 3.)

Discharge P. D. 6,500 Volts.

Distance Magnet to Reflector.	Galvanometer Deflections. 10^{-7} amp.
Negative Particles Deflected Upward.	
∞	+0.06
9.5 cm.	−0.51
6.5	.92
5.5	1.15
4.5	1.38
3.5	1.72
Negative Particles Deflected Downward.	
3.5 cm.	+0.46

TABLE V. (See Fig. 4.)

Discharge P. D. 3,000 Volts.

Distance Magnet to Reflector.	Galvanometer Deflections. 10^{-7} amp.
Negative Particles Deflected Upward.	
∞	±0
9.5 cm.	−0.05
7.5	.07
6.5	.14
5.5	.18
4.5	.28
3.5	.35
Negative Particles Deflected Downward.	
3.5	±0

These observations show three things: (1)[1] That without magnetic field the negative emission strikes the plate p, Fig. 3, and hence is not confined to a direction at right angles to the reflector and is diffuse. (2) When the negative particles are deflected away from p, Fig. 3, the deflection of the galvanometer is positive showing that there is a slight diffuse reflection of the canal rays themselves. (3) Both tables show that even with very weak fields tending to deflect the negative particles toward the plates the negative current is increased, but even the strongest field applied is insufficient to bring the negative current to a maximum. This indicates that there are particles of widely varying velocities in the emission some extremely slow and some whose velocities can not be much less than 0.2×10^{10} cm./sec. and may be very much greater.

Regarding the mechanism of the secondary radiation it is difficult to say anything with certainty. It is clear that, as the radiation takes place in a space free from any differences of potential, all parts being connected to earth, the energy not only for the separation of the negative electrodes but also for their velocity must come from the canal rays themselves unless we are willing to assume that their impact on the metal renders its atoms radioactive so that the electrons are expelled by some process of explosion. The fact that the emission of the electrons is greater at larger angles of incidence is also difficult of explanation especially in this case when the canal rays do not penetrate the metal surface and the explanation suggested by J. J. Thomson[2] for the increased emission at large angles due to cathode rays cannot apply.

We have in the emission of negative electrons by a bombardment of positive particles a condition of things very similar to that involved in the passage of negative electricity into the gas at the cathode in the ordinary vacuum discharge, as in that case also it is generally believed that the negative particles are liberated by the impact of positive particles upon the cathode. If indeed the mechanism of the two cases is the same the present work indicates means of studying the nature of this portion of the discharge in vacuum under simplified conditions.

[1] Without magnetic field the deflections in the first experiment were sometimes positive and sometimes negative.

[2] J. J. Thomson, Conduction of Electricity through Gases, p. 509.

Summary.

1. When canal rays strike an earthed metal surface there is a weak diffuse reflection of these rays.

2. There is also a diffuse emission of negative particles having widely varying velocities.

3. This negative emission increases as the angle of incidence of the canal rays increases and is probably similar in character to the secondary negative emission produced by cathode rays.[1]

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[1] Since the above was written Professor J. J. Thomson's article: Some Experiments on Kanal-Strahlen, Proc. Camb. Phil. Soc., Vol. 13, Part 4, p. 212, 1906, has appeared.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

ON THE RELATIVE PROPORTION OF THE TOTAL α-RAY ACTIVITY OF RADIOACTIVE MINERALS DUE TO THE SEPARATE RADIOACTIVE CONSTITUENTS.[1]

BY B. B. BOLTWOOD.

THE maximum α-ray activity of a considerable number of radioactive minerals was measured and compared with the activity of known quantities of pure uranium, thorium and radium. The relative decrease in activity due to the removal of known quantities of radium emanation and products of rapid change from the minerals and radium salts was also determined. The activity of the polonium and actinium separated from known quantities of minerals was compared with the activity of the uranium contained in the same minerals. From the data thus secured it is possible to calculate the relative proportion of the α-ray activity of minerals due to the separate radioactive constituents. It was found that the quantity of actinium present in minerals is proportional to the uranium contained in them, which is likewise the case with polonium when the mineral does not spontaneously evolve radium emanation. The activity due to thorium was found to be proportional to the quantity of this element contained in the mineral as indicated by chemical analysis. It was observed, however, that the specific activity of the thorium obtained from certain commerical salts of thorium was only one half that of the thorium contained in, and by certain methods separated from, the natural thorium minerals.

The general conclusions reached in the paper are: (1) That actinium is a disintegration product of uranium; (2) polonium is a disintegration product of radium through the emanation; (3) that radiothorium is a disintegration product of ordinary chemical thorium, which is elementary in character, and (4) that the α-ray activity of minerals in radioactivity equilibrium is equal to the sum of two factors, one of which depends only on the amount of uranium present and the other only on the amount of thorium contained in the mineral.

[1] Abstract of a paper presented at the meeting of the Physical Society held February 24, 1906.